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Soils as a source of bioavailable phosphorus in the Lake Whatcom Watershed

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By Scott Groce

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MASTER'S THESIS

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Scott Groce
June 10, 2011

Soils as a Source of Bioavailable Phosphorus in the Lake Whatcom Watershed

A Thesis
Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
Of the Requirements for the Degree
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Abstract

Lake Whatcom is a warm monomictic lake located east of the City of Bellingham, WA, U.S.A. and serves as the primary drinking water source for approximately 100,000 Whatcom County and City of Bellingham residents. Matthews *et al.* (2004) noted indicators of increasing algal productivity in the lake. My study quantified the amount of soluble, bioavailable, and total phosphorus in the Lake Whatcom watershed soils to help quantify the major sources of phosphorus entering the lake. In addition, I assessed the influence of soil factors (soil series, size fraction, aspect, elevation, pH, slope, percent organic matter, median particle size, and percent by volume sand, silt and clay) on bioavailable phosphorus concentrations. Organic matter, slope and elevation were found to be significantly positively correlated with bioavailable phosphorus. Total phosphorus was found to be a significant predictor of bioavailable phosphorus and produced a linear model with strong predictive capability ($\log_{10}bap = 1.39\log_{10}tp_{pers} - 1.38$; Adj. $R^2 = 0.79$; p-value < 0.001). Total suspended solids data were used to predict concentrations of total and bioavailable phosphorus contributed by the watershed; the results were compared to actual total phosphorus concentrations measured in streams. The predicted phosphorus values were lower than actual stream phosphorus values, indicating that there were additional sources of phosphorus (e.g. residential runoff) entering the lake that supplement what was contributed by watershed soils. Alternatively, the difference between measured and predicted phosphorus concentrations may be due to high variability in phosphorus concentrations within the soils. The predicted and measured phosphorus values were closest during peak storm flows, suggesting that during high flow events, most of the phosphorus transported into the lake comes from watershed soils.

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Finally, thank you to my family for believing in me when I didn't, for having as much fun bushwhacking around Lake Whatcom in the rain as I did, for grinding rocks on your vacation, for putting up with me as I navigated this rather prolonged experience, for setting me on this path before we could ever imagine where I might go.

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Introduction

Site Description

Lake Whatcom is a warm monomictic lake just east of Bellingham, Washington with a length of about 16.5 kilometers, a maximum width of about 1.7 kilometers, a maximum depth of 103 meters and a total watershed area of 14,508 hectares (Matthews *et al.*, 2009; Figure 1). The lake is the primary drinking water source for over half the population of Whatcom County, including the City of Bellingham: in total, approximately 100,000 people. The lake and parts of the watershed provide recreational opportunities as well as habitat for fish and wildlife. Eighty percent of the watershed is forestland and managed by the State of Washington or private timber companies. Other parts of the watershed are zoned residential, and there are approximately 6,500 homes currently within the watershed. Major urban development has occurred on the north and south ends of the lake, with approximately 15,000 people living within the boundaries of the watershed (City of Bellingham, 2011).

The City of Bellingham and Western Washington University have collaborated on water quality studies in Lake Whatcom since the 1960s. Current investigatory efforts began in 1988 when the City and the Institute for Watershed Studies (IWS) at Western Washington University began long-term monitoring of the lake to measure basic water quality parameters. In the 2002 - 2003 Lake Whatcom Monitoring Project Final Report, Matthews *et al.* (2004) described water quality indicators that showed that the lake's productivity was changing. Initial indications were observed in the early 1990s, including deterioration of hypolimnetic oxygen conditions, depletion of epilimnetic dissolved inorganic nitrogen, and higher epilimnetic alkalinities and pH

values due to increasing algal production. Plankton counts showed increasing densities of Cyanophyta from 1988 to the present (Matthews *et al.*, 2010).

Changing Trophic Status

Trophic status refers to the rate at which organic matter is supplied by or to a lake per unit time (Wetzel, 2001). Organic matter may be supplied by allochthonous sources, which originate within the watershed but outside the lake itself, or by autochthonous sources, which originate within the lake. Similarly, organic matter may be derived from anthropogenic sources influenced by human activity, or from allogenic sources derived from natural processes (Wetzel, 2001). Lakes dominated by allochthonous allogenic organic matter sources tend to have very low productivity as measured by nitrogen (N), phosphorus (P) and algal concentrations and are referred to as oligotrophic.

Eutrophication is a state of increased productivity and occurs as a greater proportion of organic matter is produced autochthonously. Eutrophication has been identified as a critical problem in water bodies throughout the United States (Parry, 1998; Pote *et al.*, 1999; Bennett *et al.*, 2001; Sharpley *et al.*, 1999; Sims *et al.*, 1998; EPA, 1998). The link between eutrophication of fresh waters and coastal ecosystems and phosphorus was first discussed in the United States and Canada in the late 1960s and early 1970s (Vollenweider, 1968; Lean, 1973; Syers *et al.*, 1973; Schindler, 1974). Eutrophication can result in problems in fisheries, other recreation, industry and drinking water due to increased growth of undesirable algae and aquatic plants and can cause oxygen depletion as the plants and algae senesce and decompose. Many drinking water supplies experience periodic massive blooms of Cyanophyta (Kotak *et al.*, 1993) due to the

addition of anthropogenic allochthonous phosphorus (Lean, 1973). These blooms contribute to fish kills due to low dissolved oxygen levels, and contribute to unpalatability of drinking water due to algal by-products (Kotak *et al.*, 1994). Formation of trihalomethanes such as chloroform can also occur during water chlorination as chlorine interacts with algal by-products. Many trihalomethanes are suspected human carcinogens (Palmström *et al.*, 1988).

Another indication that the trophic status of Lake Whatcom is changing is the increased amount of alum needed to treat the municipal water supply of the City of Bellingham (Matthews *et al.*, 2005). Alum or aluminum sulfate ($Al_2(SO_4)$) is commonly used by municipalities as a flocculating agent to remove suspended materials and reduce turbidity of water supplies. As alum is added to Lake Whatcom water, Al-hydroxides act as a focal point for aggregation and attract suspended organic carbon (Kopáček *et al.*, 2000), eventually forming particles of sufficient size to settle out of the water column. Greater densities of suspended carbon, such as algae, require a corresponding increase in the amount of alum necessary to reduce turbidity to local, state and federal drinking water quality standard levels. Because the algae in Lake Whatcom are increasing, there has been a significant increase (p-value < 0.001) in the alum dose required to treat Bellingham's drinking water and a significant positive correlation (p-value < 0.001) between alum dose and Cyanophyta counts between January 1994 and January 2004 (Matthews *et al.*, 2005).

The Freshwater Phosphorus Cycle

Phosphorus in lakes is derived from two major sources: those external to the lake and those internal to the lake (Figures 2 and 3). External phosphorus sources include contributions from

the atmosphere, groundwater, surface runoff and flowing waters. Atmospheric phosphorus contributions consist of precipitation and particulate fallout. Soil erosion and urban and industrial pollution can contribute to the phosphorus content of particulate fallout as dust particles become suspended in wind currents. Phosphorus content in precipitation falling in unpopulated areas is usually less than 30 μg P L^{-1} but increases to over 100 μg P L^{-1} near urban/industrial areas (Wetzel, 2001). Groundwater typically contributes only about 20 μg P L^{-1}, even in areas where soils contain large concentrations of phosphorus (Wetzel, 2001). This is the result of the insoluble nature of phosphate-containing minerals and the high demand for inorganic phosphorus by biota and soil particles. Surface runoff and flowing waters in creeks, streams and rivers are the main contributors of phosphorus to lake systems. The amount and type of phosphorus delivered via surface runoff varies greatly, depending on regional watershed characteristics such as soil series, topography, vegetative cover, quantity and duration of overland flow, land use and pollution (Keup, 1968; Vollenweider, 1968).

Major phosphorus inputs into freshwater systems consist of particulate and dissolved forms found in groundwater and surface waters from parent bedrock material, agricultural and residential land uses, sewage plant effluent, storm water runoff, and atmospheric deposition (Wetzel, 2001). Surface runoff during high-intensity storm events is the main pathway of phosphorus delivery to water (Gburek *et al.*, 2000; Catt *et al.*, 1998). Input rates vary substantially according to human activities such as land use, zoning and pollution, and geomorphic features such as watershed geology and morphology, and soil productivity. Increased runoff and turbidity from activities such as construction and logging can increase the amount of soil entering a lake (Devito *et al.*, 2000; Ramstack, 2004; Todd *et al.*, 1989). Soil particles can carry organic

phosphates derived from decomposing plant materials and inorganic phosphorus bound to iron, aluminum and calcium cations in the soil matrix. Organic matter is the main source of phosphorus in the soil environment, with concentrations of phosphorus ranging between 35 and 5300 mg P kg^{-1} and a median concentration of 800 mg P kg^{-1} (Essington, 2004). Studies of phosphorus dynamics in the North American Great Lakes region found that a small portion of sediment-bound nutrients became bioavailable because most of it is stored and buried attached to Fe- and Al-oxides (Sonzogni *et al.*, 1982; Lee *et al.*, 1979; Figure 4).

Internal delivery of phosphorus in lakes occurs in the sediments as a result of oxidation-reduction reactions at the sediment-water interface. As phosphorus enters a lake, much of it is attached to particles that immediately begin settling to the lake bottom. Inorganic phosphorus is released from the organic fraction of particles by algal and bacterial release of phosphatase enzymes in the lower waters at the sediment-water interface. In the oxidized sediments (upper 2 – 5 cm) oxidation reactions between iron and phosphate ions form amorphous iron-phosphate precipitates, removing inorganic phosphorus ions (PO_3^{4-}) that are potentially available for algal production from the water column and sediments. The reverse process occurs in anaerobic sediments located beneath aerobic sediments at the sediment-water interface. Buried organic phosphorus and amorphous iron-phosphate compounds are reduced to their ionic components, which then diffuse up to the aerobic sediments. Changes in trophic conditions in the epilimnion can affect internal phosphorus additions occurring at the sediment-water interface. When Lake Whatcom is stratified, typically May to October (Matthews *et al.*, 2010), dissolved oxygen is depleted in the overlying water in the hypolimnion in the two northern basins (Figure 1), the depth to anaerobic sediments decreases and reducing conditions predominate. Iron minerals are

reduced and dissolved inorganic phosphorus ions are released, so the sediments become a net source of phosphorus (Schlesinger, 1997; Figure 4). In the case of shallow lakes with large littoral areas and small anaerobic hypoliminia, phosphorus inputs from internal sources can account for 10 to 30 percent of total inputs (Wetzel, 2001). As a result, a substantial pool of phosphorus on inorganic particles remains potentially available to autotrophic organisms (Liang, 1994).

Forms of Phosphorus

Phosphorus can be thought of as a single pool, with different biological and physical mechanisms that vary both spatially and temporally, as it moves through the watershed and into the lake. Generally, only certain fractions of phosphorus are of concern to researchers; those fractions are defined and emphasized depending upon the researcher's interests. I selected three forms of phosphorus for analysis: soluble reactive phosphorus, sodium hydroxide-ETA extractable phosphorus, and total persulfate phosphorus. Soluble reactive phosphate (SRP) is defined in my study as the fraction of phosphorus that readily dissolves in water, naturally exists within the soil solution, and is immediately available for autotrophic uptake or adsorption onto organic metallic complexes. Sodium hydroxide-EDTA extractable phosphorus ($NaOH_{EDTA}$-P) is defined in my study as the fraction of phosphorus that is potentially soluble into solution by simultaneous extraction by sodium hydroxide (NaOH), which solublizes organic phosphorus, and ethylenediaminetetraacetic acid (EDTA), which chelates with metal cations and improves the solubility of organic phosphorus (Bowman and Moir, 1993). This method is thought to access similar phosphorus fractions as biological phosphorus extraction mechanisms (phosphatase-hydrolyzable organic phosphorus) (Turner *et al.*, 2003a). In the Lake Whatcom watershed, Liang

(1994) showed that algal populations as measured by chlorophyll *a* concentration increased in proportion with amount of soil added and then observed a similar increase in algae population with increasing additions of standard phosphate solutions (Figures A1 and A2). These results suggest a positive correlation between soil and phosphate concentrations. For the purpose of my thesis, I will call $NaOH_{EDTA}$-P "bioavailable phosphorus" (BAP). Total soil persulfate phosphorus ($TP_{pers.}$) is defined in my study as the fraction of phosphorus that dissolves under strongly acidic conditions (pH < 2) created by a solution of persulfate acid and moderate temperature (85 °C) as attained in the laboratory. Some of this form of phosphorus may be unavailable to organisms. Table 1 and Figure 5 show the form of phosphorus sampled by the methods used in my study.

Biologically available phosphorus is a dynamic form of phosphorus, composed of both dissolved phosphorus and particulate phosphorus phases derived from varying source material and affected by hydrodynamics, flow rates and bed materials (Fang *et al.*, 2002; Nikora *et al.*, 2003). Biologically available phosphorus has been identified as the form of phosphorus most responsible for eutrophication of freshwater systems (Sharpley *et al.*, 1994; Sims, 1993).

The literature suggests that total phosphorus may not be a direct predictor of phosphorus available to periphyton because algae are only able to take up soluble reactive phosphorus and phosphorus desorbable from particulate phosphorus (Ekholm and Kogerus, 1998; Reynolds and Davies, 2001). Particulate phosphorus loss from erodible soil particles can be minimized through the use of appropriate soil retention technologies, but prevention of dissolved phosphorus loss is much more difficult and is usually limited to reducing overland runoff and preventing soil

phosphorus accumulation (Sharpley, 1995).

Even though a soil may have high proportions of phosphorus present in primary or secondary mineral form, those forms of phosphorus weathered as SRP are either quickly absorbed by plants or precipitated and stored in occluded sesquioxides. Whichever course newly weathered phosphorus takes, release is slow and uptake is fast, resulting in phosphorus cycling occurring mainly within inorganic and various organic fractions (Figures 6 – 8; Williams and Walker, 1969; Walker and Syers, 1976). As a result of this rather inflexible exchange system, biota have developed a number of ways to increase soil phosphorus availability, including the secretion of carboxylates such as citric or malic acid and alkaline or acid phosphatase enzymes into the soil solution (Harrison, 1982; Lambers *et al.*, 2008), symbiosis with vesicular-arbuscular mycorrhizae (Stribley *et al.*, 1980), non-vesicular-arbuscular mycorrhizae and ectomycorrhiza (Thomas *et al.*, 1986), and interactions among microbes and fauna such as bacteria, amoebas, nematodes and earthworms (Figures 9 and 10; Coleman *et al.*, 1983; Sharpley and Syers, 1976; MacKay *et al.*, 1982).

Carboxylates and phosphatases are openly secreted into the soil solution, an aqueous liquid found within a soil normally containing ions released from mineral particles, organic matter or plant roots and leaves, by bacteria and plants, relying upon diffusion and soil solution flow gradients to encounter phosphorus containing particles, probably colloids containing occluded phosphorus attached to mineral-organic complexes. Carboxylates such as citric acid and malic acid solubilize adsorbed organic phosphorus on soil particles and phosphatases hydrolyze organic phosphorus for cotransport with H^+ across cell membranes (Figure 9). Under flow

conditions found in high slope/high elevation environments, contact time between exoenzymes and phosphorus-containing particles is lessened and phosphorus release through enzymatic action is reduced. As flow velocity decreases, as would occur in low slope/low elevation environments, contact time increases, enzymatic extraction is physically possible, and more phosphorus is made available for uptake. Mycorrhizae expand the available phosphorus volume accessible to host plants while not converting any previously unavailable phosphorus to available forms. Interactions among soil microbes and fauna have been shown to affect phosphorus availability as it is connected to substrate decomposition. Generally, as respiration (a measure of productivity) increased, so did phosphorus mineralization. Elliott *et al.* (1980) and Elliott (1986) proposed that smaller organisms such as protozoa accessed previously unavailable phosphorus sources by entering pore spaces too small for larger organisms and were then consumed by those larger organisms, thus effectively increasing phosphorus availability (Figure 9).

Concentrations of SRP, BAP, and TP_{pers} often vary according to soil series and land use. Total phosphorus concentrations in lakes can vary widely, from <5 μg P L^{-1} in unproductive waters to >100 μg P L^{-1} in highly productive waters (Wetzel, 2001). The boundary between oligotrophic and mesotrophic in the Puget Lowlands is defined at 20 μg TP L^{-1} with higher TP values used by policy-makers to recommend a lake-specific study for determination of appropriate nutrients levels to preserve characteristic land uses (Establishing lake nutrient criteria, 2003). Epilimnetic total phosphorus concentrations in Lake Whatcom prior to 2000 ranged from <5 μg P L^{-1} in the deeper basins to 5 – 8 μg P L^{-1} in the shallower basin. Since 2000, total phosphorus values have significantly increased (p-value < 0.05), but the pattern is erratic (Matthews *et al.*, 2010). Lake Whatcom has been shown to be very sensitive to even small changes in nutrient concentrations

(Matthews *et al.*, 2002; Liang, 1994). Unfortunately, mean phosphorus concentrations from lakes are a poor indicator of bioavailable phosphorus because values from all sites, depths and times are included. This is why my study will focus on soil phosphorus concentrations while constraining the sampling area to only those areas that could contribute soil particles to streams.

My study was designed to explore the relationship between soil series and bioavailable phosphorus in the Lake Whatcom watershed. Specific objectives of this study were to: 1) characterize selected physical and chemical properties of the soils of the Lake Whatcom watershed that may ultimately enter Lake Whatcom as dissolved or particulate components of runoff, 2) examine and characterize relationships between the various forms of phosphorus that could enter Lake Whatcom from the soils of the watershed, and 3) examine possible relationships between those physical and chemical soil properties analyzed and BAP.

My hypothesis was that soil series was a significant predictor of BAP, given that each soil series had unique physical and chemical properties associated with the soil series classification process that may also influence phosphorus dynamics. I thought that mean particle size would be a significant factor in the amount of BAP measured, with more BAP being found in smaller particle sizes as the larger particles would contain more unavailable phosphorus. Based on the literature, I expected organic matter, pH, slope, coarse sand, and clay to be significant factors relating to BAP.

Soil Series Descriptions

I sampled five of the most common soil types in the Lake Whatcom watershed as determined

by percent area coverage (Tables 2 – 3). Four of the five soil series I sampled were Andisols (Chuckanut, Sehome, Squalicum, and Squires series), which are derived from volcanic ash and glacial till occurring on glacially-scoured mountain slopes, hills and valleys under mixed coniferous canopy. The fifth soil series was an Inceptisol (Wickersham series) derived from alluvial fans and terraces with mixed hardwood canopies. The four Andisols were largely distinguished within the Andisol soil family by the presence or absence of an albic horizon, where clays and free iron oxides have been removed to lower horizons and the presence or absence of a spodic horizon, where those mobile clays, iron and aluminum oxides and organic carbon accumulate. Chuckanut and Squires soils had albic and spodic horizons while Sehome and Squalicum soils did not. All soil series sampled had an acidic reactivity, varying from slightly acid to strongly acid, as is common for soils in the Pacific Northwest derived from volcanic debris and influenced by large inputs of humic material (Table A1; NRCS, 2000, 2002a, 2002b, 2002c, 2004; Schaetzl and Anderson, 2005).

Andisols have unique chemical characteristics among soil orders due to rapid weathering of ash, producing amorphous or poorly crystallized iron and aluminum silicate minerals, the highly reactive nature of the colloidal fraction, and high surface area. These unique chemical properties result in accumulations of organic matter in the A horizon due to protection by aluminum-humus complexes, high affinity for multi-valent cations, and most importantly for my study, high phosphate retention (Nanzyo, 2002; Brady & Weil, 2002). Inceptisols lack enough well-defined profile characteristics to be placed in any other order but will theoretically mature according to local pedogenic processes (Brady & Weil, 2002).

Chuckanut

The Chuckanut series is composed of coarse-loamy soils, derived from volcanic ash and unconsolidated deposits of sandstone and glacial till occurring on hills and mountain slopes. The soils of this series are classified as ashy over loamy, amorphic over isotic, mesic Typic Vitrixerands, but were previously classified as coarse-loamy, mixed, mesic, Typic Haplorthods. Across northwestern Washington, Chuckanut series soils typically occur on a 15 percent southeast facing slope under a Douglas-fir canopy (NRCS, 2002a). Soil reactivity is medium acid or strongly acid (Table A1). Diagnostic characteristics of this soil series include an albic horizon from the mineral surface to 5 cm where clay and free iron oxides have been removed and a spodic horizon from 5 to 38 cm where amorphous materials composed of aluminum, organic carbon, and iron accumulate via illuviation (NRCS, 2002a; Brady & Weil, 2002).

Sehome

The Sehome series is composed of coarse-loamy soils, derived from non-compacted glacial till mixed with loess and volcanic ash occurring on glacially influenced mountain slopes and valleys. The soils of this series are classified as medial, mixed, mesic Typic Vitrixerands, but were previously classified as coarse-loamy, mixed, mesic Typic Haplorthods. Throughout the foothills of the Cascade Range of northwestern Washington, this soil series typically occurs on a 2 percent southwest facing slope under a Douglas-fir, western hemlock and red alder canopy at an elevation of 167 m (NRCS, 2004). Soil reactivity is strongly acid through slightly acid (Table A1). A diagnostic characteristic of this soil series is an ochric epipedon from the mineral surface to 5 cm, lacking stratification with low organic carbon and free iron oxide content. Another diagnostic characteristic is a cambic horizon from 5 to 66 cm with a texture of loamy very fine

sand or finer containing some weatherable minerals and alteration or removal of mineral material but little evidence of illuviation (NRCS, 2004; Brady & Weil, 2002).

Squalicum

The Squalicum series is composed of coarse-loamy soils formed in volcanic ash and glacial till occurring on glacially sculpted foothills and valleys. The soils of this series are classified as coarse-loamy, isotic, mesic Typic Haplorthods, but were previously classified as medial, mesic Andic Xerochrepts. Throughout northwestern Washington, this soil series typically occurs on a 10 percent southeast-facing slope under a coniferous canopy (NRCS, 2002b). Soil reactivity is moderately acid or slightly acid throughout (Table A1). Diagnostic characteristics of this soil series include an ochric epipedon from the mineral surface to 8 cm and a spodic horizon from 8 to 76 cm (NRCS, 2002b; Brady & Weil, 2002).

Squires

The Squires series consists of very gravelly silt loam formed in volcanic ash and slope alluvium and colluvium from phyllite and glacial till high in phyllite occurring on glacially influenced mountain sides, classified as medial-skeletal, amorphic, mesic Andic Haploxerands, previously classified as loamy-skeletal, mixed, mesic Typic Haplorthods. Throughout northwestern Washington, this soil series typically occurs on a 45 percent northeast-facing slope with a coniferous canopy (NRCS, 2002c). Soil reactivity is very strongly acid to moderately acid throughout the soil profile (Table A1). Diagnostic characteristics of this soil series are an albic horizon form the mineral surface to 3 cm and a spodic horizon from 3 - 43 cm (NRCS, 2002c; Brady & Weil, 2002).

Wickersham

The Wickersham soil series consists of alluvium from phyllite occurring on alluvial fans and terraces, classified as coarse-loamy over sandy or sandy-skeletal, mixed, super active, mesic Vitrandic Dystroxerepts, previously classified as coarse-loamy over sandy or sandy-skeletal, mixed, mesic Dystric Xerochrepts. Throughout northwestern Washington, this soil series typically occurs on a 1 percent west facing slope under a hardwood canopy (NRCS, 2000). Soil reactivity is strongly acid to slightly acid throughout (Table A1). Diagnostic characteristics of this soil series are an ochric epipedon from 5 to 23 cm and a cambric horizon from 23 to 66 cm (NRCS, 2000; Brady & Weil, 2002).

Methods

All field measurements and water quality analyses were done using standard methods as described below and summarized in Table 4. Table 4 also lists abbreviations and units used to describe water quality and physical analyses in this document.

Sampling Plan

Sampling locations were selected using a stratified random sampling plan. The Lake Whatcom watershed was divided into 44 groups according to soil series as determined by NRCS classification (Soil Conservation Service, 1992). Five out of 44 soil series were randomly selected for sampling, not weighted by area, comprising approximately 50% of the watersheds' area and roughly covering the geographical extents of the watershed (Table 3). Sample areas were created within each selected soil series using GIS software to identify NRCS-identified soil series within

45.72 m (150 ft) of a perennial stream channel and 402 m (one-quarter mile) of a road (Figure 11). Sampling points were based on on-site feasibility determinations. Sample size was determined based on achieving a balanced statistical sample between soil series, sampling effort (the amount of resources required to collect further samples), and site accessibility.

Duplicate samples were collected in the field at stratified randomly selected locations to the level of 10% of total sample size. Duplicate samples were collected to provide quality control field duplicates and were processes and stored using methods identical to non-duplicate samples.

Sample Collection

Global positioning system (GPS) coordinates were recorded using a Trimble Geosystems 3 hand-held unit at each sampling site (Trimble, USA). Global positioning system points were differentially corrected upon analysis to reduce horizontal error associated with each point to approximately 1 – 2 meters. Surface morphometry properties including elevation, slope aspect, and slope gradient were recorded at each sampling location (Soil Survey Staff, 2002). Five samples were collected within a 28-m^2 area centered at each sample location and combined into a composite site sample (Figure 12). Above-ground vegetation was removed, and the top organic soil fraction was collected and returned to the lab (Soil Survey Staff, 2004). Mineral soil samples were collected using a coring device to a depth of 10 cm because it extends below the plowing depth to undisturbed soil layers and includes the majority of the root biomass (Soil Survey Staff, 2002; Robertson *et al.*, 1999). Five samples were collected within a 28-m^2 area centered at each sample location and combined into a composite site sample (Figure 12).

Sample Storage

Samples were collected and placed into paper grocery bags, transported to the lab and air dried at ambient laboratory temperatures. Air-dried samples were sieved (see below) and then stored in low-density polypropylene bags at ambient laboratory temperatures until analysis.

Size Fraction

Each composite sample was sieved using a Ro-Tap Sieve Shaker (Laval Lab Inc., Laval, Quebec, Canada) for 20 minutes into three size fractions based on diameter (d), reflecting ecologically significant size classes: small ($d < 0.50$ mm) representing medium sand, silt and clay; medium ($0.50 \text{ mm} \geq d \leq 2.0$ mm) representing coarse sand; and large ($2.0 \text{ mm} > d \leq 75$ mm) representing gravel and stone (NRCS, 2010).

Aspect

Aspect was measured in the field and was the compass direction in degrees that the slope faced upon sample collection as determined by the sample collector. Aspect values were transformed from degrees into radians for statistical analysis using the formula:

$$\text{Radians} = \text{Degrees} \times \frac{\pi}{180}$$

Elevation

Elevation was measured in the field and was the height above mean sea level in meters from the central coring location at each sampling site, as determined by repeated GPS location logging

over the time spent collecting samples and other relevant data. Elevation is considered a sub-factor of the relief factor, being of increased importance in mountainous terrain. Higher elevations are expected to correspond to steeper slopes and more phosphorus.

Slope

Percent slope was measured in the field using a clinometer. Jenny (1941) considered slope to be a sub-factor of the relief factor but may influence parts of many other factors and sub-factors contributing to soil forming processes. Aspect and slope interact to affect freeze-thaw activity, leading to mass movement and creation of gentler slopes. Younger soils are expected to be present on less stable slopes.

Bulk Organic Matter

Soil organic matter was measured using the loss-on-ignition method as outlined in the Soil Survey Laboratory Methods Manual following NRCS methods (NRCS, 2010). The loss-on-ignition method uses a muffle furnace at high temperature (400°C) over an extended period of time (16 hours) to ash all the organic matter, leaving behind plant ash and mineral material. Percent loss-on-ignition was calculated using the formula:

$$\%\ \mathrm{LOI} = \frac{(\text{weight of crucible} + \text{sample}) - (\text{weight of crucible} + \text{sample after ashing})}{(\text{weight of crucible} + \text{sample}) - (\text{weight of empty crucible})} \times 100$$

pH

Measurements were taken following methods outlined in Robertson *et al.* (1999) using a 1:4 or 1:6 soil to water mixture of 5 grams wet weight soil and either 20 mL or 30 mL distilled

deionized water and a glass electrode. The amount of water added depended upon the amount needed to submerge the electrode. Measurement of pH was performed within 48 hours of sample collection to avoid pH changes resulting from biological activity (Robertson *et al.*, 1999). Samples that could not be analyzed within 48 hours were stored in a freezer. These results were flagged; statistical analysis indicated that these samples were not significantly different than those samples analyzed within 48 hours of collection (two-sample Kolmogorov-Smirnov test; p-value = 0.812; Figure A3).

Particle Size Distribution

Samples were sieved to a grain diameter of 500.0 µm or less. A suspension of the sample in distilled deionized water was measured with a Malvern Mastersizer 2000 laser particle sizer (Malvern, UK) equipped with a Hydro 2000G sample dispersion accessory. The grain size distribution was expressed as the measured volume divided into fractions logarithmically spaced between 0.1 and 500.0 µm, with the median value calculated for statistical analysis (Sandström *et al.*, 2005).

Sand

Sand is primarily composed of rock fragments and primary minerals and is therefore chemically inactive. Sand particles directly affect soil porosity and other properties related to water (NRCS, 2010). Percent sand by volume was determined by laser particle size distribution analysis as that fraction of sediments between 50 µm and greater. All samples were sieved to 500 µm prior to analysis, but some slightly larger sediment may have passed through the sieve resulting in the inclusion of a small amount of particles greater than 500 µm in size.

Silt

Silt is primarily composed of primary minerals, particularly quartz, and has low chemical activity. Soil particles fill voids between sand grains and slow water and air movement (NRCS, 2010). Percent silt by volume was determined by laser particle size distribution analysis as that fraction of sediments between 2 μm and 50 μm in size.

Clay

Percent clay by volume was determined by laser particle size distribution analysis as that fraction of sediments less than 2.0 μm to 0.5 μm in size.

Phosphorus

Soluble reactive phosphorus (SRP) was extracted from a distilled water suspension of 5 grams of soil in 50 mL water. Samples were shaken for 1 hour at 150 rpm on a VMR DS-500 orbital shaker (VWR International, Vienna, Austria) and centrifuged in an IEC HN-SII centrifuge (Thermo Fisher Scientific, Waltham, MA, USA) for 20 minutes at 2500 rpm to obtain a clear supernatant. The supernatant was filtered through acid washed GF/C glass microfiber filters (Whatman Inc., Piscataway, New Jersey, USA) and analyzed according to the procedures outlined in the IWS Standard Operating Procedures #19 (IWS, 2004) on an Alpkem FS3000 autoanalyzer (Alpkem Corporation, College Station, Texas, USA).

Sodium hydroxide-EDTA extractable phosphorus (BAP) was extracted in a suspension of 0.25 g soil and 50 mL extracting solution of 0.25 *M* NaOH and 0.05 *M* Na_2EDTA. Suspensions were

heated to 85° C for 2 hours in a VWR 1330 oven (VWR International, Vienna, Austria). Suspensions were then centrifuged for 20 minutes at 2500 rpm and clarified by filtering through acid washed GF/C glass microfiber filters (Whatman Inc., Piscataway, New Jersey, USA).

Total persulfate phosphorus (TP_{pers}) was determined by digesting 0.5 g soil in 50 mL potassium persulfate and 11 *N* H_2SO_4 as summarized in APHA (2005). Suspensions were placed into a Tuttnauer-Brinkmann 3850E digital autoclave sterilizer (Tuttnauer USA Co. Ltd, Hauppauge, NY, USA) for 35 minutes at a maximum pressure of 18 PSI and a maximum temperature of 121° C. Suspensions were then centrifuged and filtered in the same manner as $NaOH_{EDTA}$-P samples.

Soluble reactive, $NaOH_{EDTA}$ extractable, and total persulfate phosphorus were measured as inorganic phosphate using the ascorbic acid method (APHA, 2005). Extracted $NaOH_{EDTA}$-P and TP_{pers} samples were diluted 100 times (i.e. 0.5 mL extract per 50 mL diluted solution) for analysis according to the ascorbic acid method (Bowman and Moir, 1993; Lajtha *et al.*, 1995; APHA, 2005) on a Milton Roy Spectronic 21D spectrophotometer (Milton Roy, Ivyland, PA, USA). Final phosphorus concentrations were calculated using the adapted formula (Lajtha *et al.*, 1995):

$$\text{mg P per kg soil} = C \text{ x } D.F. \text{ x } F \text{ x } 1/1000$$

where

C = concentration of P in extract solution as µg P per mL extract

$D.F.$ = dilution factor as mL extract per mL sample solution

F = mL extract per g dry soil

Table 1 shows the theoretical fractions of phosphorus digested or extracted by these methods.

Statistical Analysis

Data were analyzed using conventional univariate, bivariate and multivariate statistics to evaluate potential relationships among variables. Parametric assumptions were tested, and the data were either transformed or nonparametric tests were used if the data failed to meet assumptions of normal distribution and homoscedasticity. Samples were assumed to be independent from each other given the use of a stratified random sampling design where a predetermined number of randomly created sample locations meeting previously outlined criteria were generated using a random number generator. Results were plotted and analyzed graphically to look for basic patterns in the data and compared to known groupings such as soil series and size fraction. Simple descriptive statistics were used to describe each group of data across soil series and size fraction. If initial statistical investigations indicated possible relationships between variables, correlation analysis using Kendall's τ was used to quantify such relationships. If a strong correlation was identified, linear modeling was used to describe those relationships (R Development Core Team, 2010).

To address the assumptions of parametric statistical procedures, various mathematical transformations were attempted to bring the empirical distributions of many of the variables closer to a theoretical normal distribution. When transformations were not able to correct deviations from the standard normal distribution, samples distributions were either assumed to approach normality due to large sample sizes (n = 195) or appropriate non-parametric statistical

procedures were used. All phosphorus measures were $\log_{10}$ transformed, and percent organic matter, silt and clay were square root transformed. Transformed values for SRP and TP_{pers} were first analyzed using a two-factor ANOVA. Significant relationships were used to create a predictive linear regression equation for BAP with confidence and prediction intervals describing the error associated with observed and predicted BAP values. Additionally, transformed data were analyzed using single factor ANOVA and Tukey multiple comparison tests using Holm's correction for repeated measures (Holm, 1979) with p-value ≤ 0.05 to identify differences within soil series and size fraction. Results from statistical analyses are included in the appendix (Tables A1 – A9; Figures A3 – A29).

Results and Discussion

Soil Series

When grouped by soil series, the soils in the Lake Whatcom watershed represented a range of slopes, elevations and aspects (Table A1) All five series had slightly acidic soils (range of median pH values = 4.93 – 6.2) and were composed of approximately 20% silt, 80% sand and 1% clay (range of median values, respectively, was 17 – 21%, 78 – 82%, 0.48 – 1.17%). The median particle size was around 300 mm (range of medians = 292 – 335 mm) and the median organic matter was approximately 3% (range of medians = 2.50 – 3.44%). Regardless of soil series type, the soils had a median SRP concentration of about 1 mg P kg^{-1} (range of medians = 0.42 – 1.03). The Wickersham soils had slightly less BAP compared to the other soil series (Wickersham median = 207; other medians = 319 – 558) and the Squires soils had slightly more TP_{pers} (Squires median = 959; median range for other series = 619 – 692). Analysis of variance detected

significant differences between soil series types for some of the analytes, but there was no consistent pattern associated with soil type (Tables A5 and A6; Figures 13, 15, A4 – A5).

Size Fraction

As with the soil series, when the soil samples were partitioned according to size fraction, the groups represented a range of slopes, elevations and aspects, with all groups having slightly acidic soils composed of approximately 20% silt, 80% sand and less than 1% clay (Table A2).

Analysis of variance detected significant differences among size fractions for organic matter and TP_{pers} concentrations (Table A8; Figures 14, 16). When pairwise comparison analysis using Holm's correction was performed, the "large" size fraction ($d > 2.0$ mm) was significantly different than "medium" and small size fractions ($0.5 \text{ mm} < d < 2.0$ mm; $d < 0.5$ mm, respectively; Table A9). Pairwise comparison analysis also showed that there was more TP_{pers} in the large and medium size fractions compared to the small size fraction, but no difference between large and medium size fractions (Table A9).

The large size fraction may have had significantly less organic matter than the other two size fractions due to several factors surrounding the nature of sample collection and processing. According to previously outlined sampling protocols, the organic layer, which is composed of organic matter in various stages of decomposition, was manually separated from underlying mineral soil layers (commonly the A horizon) along what was usually a clear boundary. As a result, large pieces of organic matter that would have been included in the large size fraction because they had diameters over 2 mm were purposefully excluded as they were not really part

of the soil column. Smaller pieces of organic matter that were missed in the exclusion process may have been able to pass through the sieves used to separate the size fractions. Additionally, the sieving process itself may have physically broken larger pieces of organic matter into smaller pieces due to the motion of the sieve shaker, causing those smaller pieces to pass through the smaller sieves and be classified in a different size fraction. Furthermore, the loss-on-ignition method calls for the use of porcelain crucibles that have a finite size and shape. Relatively large pieces of organic matter may have been unintentionally excluded simply because they were too big to fit in the crucible during analysis, while pieces of organic matter in the medium and small size fractions had roughly the same chance of selection for analysis as any other particle in the sample. The small size fraction may have had less TP_{pers} than the medium or large size fractions due to the process of aggregation whereby smaller soil particles are biologically or physically cemented to other particles of varying sizes. Total persulfate phosphorus contained in the interior of these particles, or in areas excluded from contact with the soil solution, would be more protected than in smaller sized soil particles.

Laser particle size distribution analysis found that most particles in the small size fraction were classified as fine or coarse sand (~80%), while most of the remaining particles were classified as silt (~20%) and only ~1% were classified as clays. Analysis of variance did not detect any significant differences among soil series among sand, silt or clay variables. Analysis of variance and multiple comparison testing did detect significant differences in median particle size between Sehome and Squires soils, and between Sehome and Wickersham soils (Table A6). Squires and Wickersham soils had a larger median particle size possibly due to the presence of channery fragments of phyllite up to 15 cm in diameter that had not been weathered as much as

those materials within Sehome soils, which contain gravelly particles up to 7.6 cm in diameter.

Total persulfate phosphorus and SRP were positively correlated with median particle size (τ = 0.169 and 0.202, respectively, p-value < 0.05). Squires soils had significantly more TP_{pers} than other soil types and had the largest particle size. This indicated that the amount of phosphorus delivered and ultimately made available as inorganic phosphate was positively influenced by the size of soil particle delivered, possibly according to a mechanism similar to that described in Sharpley (1985). Sharpley found that high rainfall intensity (> 11 cm h^{-1}) and high slopes (> 8%) increased soil disturbance to the point that entrained soil material became the main factor accounting for soluble phosphorus transport in runoff. Further considerations of the sources and influences on available phosphorus must include particle size as it partially determines SRP, TP_{pers} and, ultimately, BAP.

Soil Age

The role of repeated glacial scouring and deposition events 20,000 years ago to 10,000 years ago in "resetting" the geologic clock throughout northwestern Washington should not be ignored as a key event in soil formation. Not only were sediments extensively transported, sometimes over large distances, and mixed, but remaining bedrock materials were buried under several hundred meters of glacial till. This effectively stopped any contribution those bedrock materials may have made to soil formation through chemical or physical weathering. However, there are locations with exposed bedrock material throughout the watershed depending on slope and the influence of water. Areas with a large slope gradient would not be able to accumulate much material before the slope becomes over-steep and the material slides down slope. Surface water

influences soil formation through physical erosion; continuously moving soil particles downstream. Groundwater can also be influenced by bedrock materials, transporting dissolved minerals that filter through the soil column to lakes and streams.

Soil chronosequences that connect soil age and physical or chemical properties do not currently exist for the Lake Whatcom watershed, despite the fact that this would be essential information for further refinement of the results of my study. Local geomorphology may mask glacial influence through topography, slope and sediment transport processes. A detailed description of site geomorphology was not performed for my study but may be appropriate for further clarification of the results of my study. Without more precise analysis of soil age, statistical analysis of a soil age variable is meaningful. Therefore, this variable was not included in my study. Future studies may show it to be an important predictive factor of soil phosphorus availability upon further analysis.

Relationships between SRP, TP_{pers} and BAP

Bioavailable P was positively correlated with SRP and TP_{pers}, and, to a lesser extent, positively correlated with elevation, organic matter, and slope (p-value < 0.05; Table 5; Figures 17 – 21). In the Lake Whatcom watershed, soluble reactive phosphorus values were 50 – 100 times less than BAP and TP_{pers} values, and TP_{pers} values were generally twice BAP values. Median SRP was 0.09% that of median TP_{pers}, median BAP was 53% of median TP_{pers} (Tables A1 and A2; Figure 13). Bioavailable phosphorus was significantly correlated to both SRP and TP_{pers}, but more strongly correlated to TP_{pers} (τ = 0.407 and 0.695, respectively; Table 5; Figures 17 and 18).

My phosphorus results closely matched the results from a previous study performed within the Lake Whatcom watershed by Liang (1994). Liang (1994) sampled construction spoils composed of Whatcom silt, Nati loam and Squalicum gravelly loam in the Austin Creek watershed, a secondary stream flowing into Lake Whatcom. Liang measured almost identical amounts of SRP, BAP and TP_{pers} as I did even though different soil types were analyzed (Table 6).

My study also produced results similar to several studies from sites that were not located in the Lake Whatcom watershed, but measured analogous soil phosphorus fractions using methods similar to mine (Table 6). Turner and Engelbrecht (2011) assessed 19 lowland tropical forest soils from Panama for soil organic phosphorus composition. They found a slightly higher TP_{NaOH}:BAP than was found in my study, indicating slightly more TP_{NaOH} than BAP_{NaOH}. One of their conclusions was that total phosphorus was the primary control on the concentration of soil organic phosphorus, but the relative percentage of total phosphorus in organic form was related to vegetative demand for phosphorus. Ultimately, they concluded that acidic soils may account for accumulations of phosphate diesters in soil organic phosphorus forms.

Dou *et al.* (2009) examined 10 agricultural soils from Pennsylvania that had received manure application for 8 or more years. They found a range of TP_{NaOH}:BAP_{NaOH} ratios in untreated soils, that were within the range of TP_{NaOH}:BAP_{NaOH} ratios observed in my study, and a lower range of TP_{NaOH}:BAP_{NaOH} ratios in manure treated soils. They concluded that potential phosphorus release from manure treated soils was 3 to 30 times greater than in untreated soils.

Zhang *et al.* (2009) collected surface sediments (10cm) from seven lakes representing two

ecological zones in China: the lower and middle reach Yangtze River regions and the Southwestern China Plateau. They found a gradient of TP_{NaOH}:BAP_{NaOH} ratios corresponding to degree of lake eutrophication, which were slightly less than most Lake Whatcom watershed soils. Squalicum and Chuckanut soils had the most similar TP_{NaOH}:BAP_{NaOH} ratios to those found by Zhang *et al.*

Turner *et al.* (2003b) sampled 18 semi- arid arable soils to 30-cm depth from locations throughout the western US. Turner *et al.* reported TP_{NaOH}:BAP_{NaOH} ratios similar to what I measured in the Lake Whatcom watershed. They concluded that organic phosphorus concentrations in semi-arid soils were controlled by complexes made with the soil matrix and the biological demand for phosphorus.

Bioavailable Phosphorus and Organic Matter

Organic matter can be either a sink or a source of organic phosphorus. Organic matter acts as a source of BAP through hydrolyzation of labile organic phosphate adsorbed onto the surface of organic matter as soluble reactive phosphorus (inorganic phosphate) pools are depleted. Phosphorus mineralization (organic phosphorus to inorganic phosphorus) was found to be controlled by inorganic phosphorus availability and phosphorus demand of biomass, and by mineralization of organic matter which releases organic phosphorus as a by-product. Organic matter acts as a sink of soluble organic phosphorus through immobilization, which is controlled by the availability of inorganic phosphorus and organic substrates that grow and maintain soil biomass. Iron and aluminum phosphates have also been found to act as phosphorus scavengers, drawing free or weakly bound phosphate ions into low solubility complexes which effectively

remove increasing amounts of phosphate from the system as the soil ages (Essington, 2004).

Organic matter is a major route for recycling of organic phosphorus, being composed of inorganic solids, decomposed plant materials such as tannins and lignins, cellular debris, and aggregates of these compounds. Stewart and Tiessen (1987) found that most organic soil phosphorus was contained in the reactive side chains of soil organic matter. In fact, inositol phosphorus compounds with humic acids, fulvic acids or metal complexes can be further differentiated according to turnover rates. Fulvic-acid-associated phosphorus was found to be largely composed of recently delivered organic matter and plant litter while humic-acid-associated phosphorus tends to turn over more slowly (Stewart and Tiessen, 1987). Metal complexes such as aluminum and iron sesquioxides influence soil organic phosphorus through occlusion processes, which chemically sequester inorganic and then organic phosphorus. The dynamic relationship between BAP and organic matter is important because at any point in time, organic matter can either be adding to or taking away available phosphorus depending on pH, the amount of inorganic phosphorus already in solution, and the age of the soil (Figures 6 and 7).

In the Lake Whatcom watershed, bioavailable phosphorus was positively correlated with organic matter (Figure 19; Table 5; $\tau = 0.192$; p-value < 0.001). This relationship suggests that organic matter acts as a phosphorus buffer in soils, adsorbing and storing phosphorus in times of excess inorganic phosphorus input compared to biological demand or strongly acidic or basic conditions, and releasing phosphorus in times of extremely low inorganic phosphorus input and optimal soil reactivity conditions for plant growth. Organic matter content was approximately

3% across all soil types and size fractions. This is considered low, but not so low as to affect plant growth (e.g. Lickacz and Penny, 2001). An organic matter management guide for farmers estimates that one acre of crop plants grown on soil with 3% organic matter may obtain 2.7 kg of phosphorus from that organic matter over the course of one year in the state of Minnesota (Regents of the University of Minnesota, 2002). The link to increasing organic matter and plant productivity (and phosphorus) is not linear and is difficult to tease apart from the other factors that affect and influence productivity. Increasing organic matter to very high levels, 8% for example, would not necessarily affect plant productivity the way it would if organic matter were to decrease to a very low level (e.g. less than 2%). Excess organic matter may accumulate in wetland systems where decomposition rates are dramatically slowed due to low-oxygen conditions and large amounts of phosphorus are stored in poorly decomposed plant material. Excessive reduction of organic matter in the Lake Whatcom watershed would also have a negative effect on phosphorus availability due to reduced infiltration and aeration, increased evaporation, decreased water holding capacity, increased crusting, reduced root development and aggregation, and increased soil compaction (Regents of the University of Minnesota, 2002).

Bioavailable Phosphorus and Slope

Increasing slope corresponds to increasing erosion potential and increasing sediment transport away from the site. This can increase BAP because SRP is exported in runoff and must be locally replenished from particulate and occluded forms. To reestablish phosphorus sorption equilibrium, some loosely bound phosphorus is transformed to SRP by simple diffusion gradients. Transformation by diffusion is faster than any other form, but a minute amount of phosphorus actually exists in this easily diffusible form in the soil solution. Slope is probably

most important to BAP in that it is the factor most directly related to physical transport of soil solution and sediments. Plants and other biota can access more tightly bound phosphorus pools through exoenzymes and mycorrhizal symbiotic relationships, bringing more phosphorus into the terrestrial phosphorus cycle, but it is much less energetically expensive to focus on retaining and efficiently cycling phosphorus already in organic forms.

Bioavailable phosphorus concentration was positively correlated with percent slope in Lake Whatcom soils (Table 5; Figure 20; $\tau = 0.173$; p-value < 0.001). In the Lake Whatcom watershed, the mean slope was 27% (Table A3), which is classified as moderately steep by the NRCS (Soil Conservation Service, 1992). Such steep slopes throughout the Lake Whatcom watershed would result in the transport of suspended sediments to the lake. Additional study would be necessary to describe this relationship in the Lake Whatcom watershed, and should include factors such as discharge, precipitation, and elevation. Regardless of the specific impact of these factors on the fundamental relationship between slope and suspended solids, it would be important to focus management efforts on reducing runoff from areas with steeper slopes. This effect would be somewhat mitigated by low slope areas that could act as a temporary sink for suspended sediments. However, the net flow of sediments would be towards the lake.

Bioavailable Phosphorus and Elevation

Elevation operates in a similar manner as slope, as a physical factor responsible for transporting phosphorus down slope through gravity. Phosphorus concentrations at a specific elevation may also be affected by microclimatic factors such as temperature and humidity that affect mineral weathering rates and soil formation processes. Bioavailable phosphorus was positively correlated

with elevation in Lake Whatcom soils ($\tau = 0.129$; p-value = 0.01; Table 5; Figure 21). In the Lake Whatcom watershed, mean elevation was 165 meters above mean sea level (Tables A1 and A2). The results of correlation analysis indicated that sediment control needs to be especially rigorous on steep areas of high elevation, although this relationship between slope and elevation is intuitive.

Slope and elevation work together to transport sediments into streams and ultimately into Lake Whatcom, constantly removing existing SRP from a site and creating a gradient favoring the transformation of weakly held organic phosphorus to soluble inorganic soil phosphorus. Organic matter acts as a type of mediating factor between the phosphorus released by decomposing organic matter, phosphorus contained in the soil solution, and phosphorus required by biota. Organic matter can also somewhat mediate the effect of steep slopes by absorbing water, holding the soil matrix together, and acting as a substrate for the transformation of SRP into unavailable organic forms.

Principal Component Analysis

Principal components analysis is an ordination technique used to help show relationships between correlated variable in multivariate data. I used principal component analysis (PCA) because there were strong correlations among the phosphorus variables and significant but lower correlations with other variables. I tried a PCA to see if the multivariate approach provided more insights into the data than simple bivariate correlations (see Appendix for a more thorough discussion of PCA).

Three-Factor PCA: Phosphorus Variables

I started my analysis by creating an ordination using just the phosphorus variables because correlation analysis indicated that the phosphorus variables were more closely related to BAP than any other variables (Table 5). Principal component analysis partitioned 79% of sample variance into the first component when the PCA was built using only the three phosphorus variables (n = 195; Table 7). Bioavailable phosphorus, SRP and TP_{pers} were placed in roughly the same location along first and second components, which is not surprising because there was a strong positive correlation among all three of these variables. Soluble reactive phosphorus was separated from BAP and TP_{pers} by differences in the second component, suggesting that of the three variables, TP_{pers} and BAP were more similar to each other than either was to SRP (Figure A10). The PCA did not reveal any obvious relationships within BAP, SRP and TP_{pers} that could be attributed to soil series or size fraction (Figures 22 and 23).

Eight-Factor PCA: Phosphorus and Water Quality Variables

I followed the 3-factor PCA with an ordination based on all the measured variables except those with data only in the "small" size fraction. I wanted to see if the additional variables would provide insights into the relationships between variables and whether the higher order ordination could identify relationships related to soil series or size fraction. When aspect, elevation, organic matter, pH, and slope were included in the principal component analysis (with SRP, BAP and TP_{pers}) the amount of variation explained by first component decreased to 32% (n = 195; Table 8). The eight-factor PCA did not provide much additional insight into the relationship between variables and the samples still did not ordinate into distinguishable groups based on soil series or size fraction (Figures 24 and 25). This indicates that models using just TP_{pers}, with the possible

addition of SRP, might be sufficient for predicting BAP.

Various forms of phosphorus composed the first component in the eight-factor PCA, so the first component could be labeled "P." The second component could be called "relief" because it was largely a combination of slope and elevation. The variables composing the first and second components were also the only variables significantly correlated with BAP. My analysis indicated that, although TP_{pers} may be the most important variable, relief was the most important combination of physical variables that influenced BAP. The third component was made up of aspect and pH and was more difficult to characterize. Aspect can influence microclimatic factors such as precipitation and temperature, which would in turn influence soil pH. The correlation among the two factors was weakly positive, but the lack of any specific relationship was not surprising because the structure of PCA is to place the best explanatory variables in the first few components (Table 8), portioning weaker variables into higher (e.g. 3rd) components.

Twelve-Factor PCA: Phosphorus and Water Quality Variables - Small Size Fraction

Principal components analysis requires that all variables are measured for each sample that is included in the analysis (i.e. no missing values in the row). The only particle size that also had laser size distribution measurements was the small size fraction. To check whether particle size influenced the ordination, I did a 12-factor PCA using the variables with data in the small particle size (n = 65; factors: aspect, elevation, om, ph, psd, sand, silt, clay, slope, srp, tp, bap). This produced a slightly weakened PCA compared to the eight-factor PCA (Table 9), and there was still no clear influence of soil series (Figure 26).

Total persulfate phosphorus and BAP were tightly grouped, with SRP slightly separated. Particle size, organic matter and sand were loosely grouped along the positive portion of the first component, approximately orthogonal to SRP, BAP, and TP_{pers} indicating that there were significant correlations among those variables. Aspect, pH, and elevation were all closely clustered indicating a significant correlation among those variables (Table 5). Clay and silt variables were grouped along the negative portion of the first component, indicating no significant correlations between those variables and the phosphorus measures. In summation, the phosphorus measures ordinated together; pH, aspect, and elevation ordinated together, with slope loosely ordinated near those variables; particle size and organic matter loosely ordinated; clay and silt loosely ordinate; and sand did not ordinate with any other variables.

The first component of the 12-factor PCA was strongly influenced by fine particulates (silt and clay). This result was surprising because silt and clay were not significantly correlated with BAP, despite evidence in the literature linking small particles to phosphorus content (He *et al.*, 1995). The second component was most affected by forms of phosphorus (SRP and TP_{pers}, but not BAP). This result makes sense in light of the first component being primarily composed of fine particulates. Due to the nature of PCA, the second component would be composed of those factors most different from the factors used in the first component. The third component contrasted aspect and elevation to pH and could be labeled "Microclimate" (Table 9). The results of this PCA suggest that fine particulates may indeed be an important factor, but this result can only be applied to the data within the small size fraction.

Regression Analysis

Total persulfate phosphorus and SRP values were used to construct two predictive linear models for BAP. These two variables were selected because PCA indicated that other variables did not increase prediction of BAP. One model was created to predict BAP as a function of TP_{pers} (Equation 1); a second model was created using TP_{pers} and SRP to predict BAP (Equation 2). The three variables did not meet all the assumptions of parametric statistics (Tables A3 – A5), so TP_{pers}, SRP and BAP were $\log_{10}$ transformed in Equations 1 and 2 to minimize the potential bias of heteroscedastic sample variances on estimates of sampling error, addressing the assumption of parametric statistics that could most affect model accuracy (Table A2).

Equation 1. $$\log_{10} \mathrm{bap} = 1.39 \log_{10} \mathrm{tp_{pers}} - 1.38$$

Equation 2. $$\log_{10} \mathrm{bap} = 0.55 \log_{10}(\mathrm{tp_{pers}} + \mathrm{srp}) + 1.31$$

The adjusted R^2 of Equation 1 was 0.79, meaning that the regression equation accounted for approximately 79% of the variation seen in the dependent variable (p-value < 0.001). Figure 27 shows the theoretical single-variable regression line (Equation 1) plotted against experimental data with 95% confidence and prediction intervals. Figure 28 shows a simple plot of residual values plotted against fitted values for the single- variable model. The residuals were evenly distributed on the horizontal line at y = 0, which indicates that although the variables did not meet all the assumptions for parametric statistics, there was no consistent bias in the linear model. Table 10 shows BAP predicted using Equation 1 with minimum, median and maximum observed TP_{pers} values compared to measured BAP. Predicted BAP closely matched measured BAP, especially for predicting lower BAP values.

The adjusted R^2 of Equation 2 was 0.62, meaning that the inclusion of an additional variable lowered the predictive capability of the model compared to the single- variable model (p-value <0.001). Figure 29 shows the theoretical two-variable regression line (Equation 2) plotted against experimental data with 95% confidence and prediction intervals. Figure 30 shows a plot of residual values plotted against fitted values for the two-variable model. The residuals were evenly distributed on the horizontal axis, indicating that they did not introduce bias into the linear model. Table 10 shows predicted BAP using Equation 2 from minimum, median and maximum measured TP_{pers} compared to measured BAP. The bivariate model (Equation 2) over-estimated BAP compared to measured BAP values. Equation 1 produced more accurate estimates of BAP, using a simpler expression, so Equation 1 is the preferred model. Based on this analysis, I determined BAP can be modeled as a simple function of TP_{pers}.

Predicted Phosphorus from Total Suspended Solids

The results from Equation 1 show that we can predict BAP from TP_{pers}. The literature suggests that we should also be able to predict TP_{pers} from total suspended solids (TSS), which would allow us to estimate BAP from TSS. The Institute for Watershed Studies has been measuring TSS, TP_{pers} and SRP values from streams within the Lake Whatcom watershed as part of their water quality monitoring program since the early 1980s. I was interested in how those data compared to the predicted TP_{pers} and BAP values generated from my data. Total suspended sediments data from IWS were used to predict the amounts of TP_{pers} and BAP that would be estimated from soil inputs. These values were then compared to measured concentrations of stream SRP and TP_{pers}. The data were obtained from the IWS Silver Beach

Creek sampling station, located in the urbanized northern part of the watershed, during one storm event in November 2009 (R. Matthews, personal communication, Figure 31).

Total suspended sediments measured by IWS staff in the creek ranged between 6.82 mg sediment L^{-1}, corresponding to the lowest flow, and 257.97 mg L^{-1}, corresponding to the sixth highest flow, and first peak flow after the beginning of the storm event. Total persulfate phosphorus estimated from TSS using the stoichiometric relationship between soil and TP_{pers} was between 4.5 µg P L^{-1} and 171.3 µg P L^{-1} (Figure 32; Table 11). The difference between estimated TP_{pers} concentrations and stream TP_{pers} concentrations ranged between -4% and -85%. The estimated TP_{pers} concentrations matched stream TP_{pers} concentrations more closely when the concentration of TSS was highest, ostensibly during periods of peak flow. Using TSS to predict stream TP_{pers} and Equation 1 to predict BAP as a function of TP_{pers} resulted in BAP estimates ranging from 0.3 µg P L^{-1} to 53.1 µg P L^{-1}. Predicting stream BAP as a function of measured stream TP_{pers} using Equation 1 lead to BAP concentrations ranging between 4.6 µg P L^{-1} to 66.2 µg P L^{-1} and an underestimation of BAP concentration at every time interval.

Based on my results, roughly twice the amount of TP_{pers} and BAP flowed into Lake Whatcom than was accounted for by my simple model (Table 11). This difference may be due to natural variation of phosphorus concentrations within soils or phosphorus may be entering the lake by other routes. These sources may be natural or anthropogenic as outlined earlier (Bedan and Clausen, 2009; Carpenter *et al.*, 1998; Devito *et al.*, 2000, etc). Stream phosphorus is a composite of all possible inputs, including portions of the watershed I did not sample, and my soil phosphorus represents a composite sample of a relatively small area from five soil series.

Consequently, soil phosphorus may be an underestimate of phosphorus when considered in the context of stream phosphorus, while stream phosphorus may be an overestimate of phosphorus when considered in the same context as soil phosphorus.

Lake Whatcom Management Implications

One of the most important implications from my research is that a significant portion (approximately half) of the TP_{pers} in soils in the Lake Whatcom watershed is potentially available to biota. The relationship between from TP_{pers} and BAP was independent of soil type and BAP can be predicted as a simple linear function of TP_{pers}. These findings are important for the management of the Lake Whatcom. Care should be taken to control disturbed sediments, especially during the winter storm season when a majority of annual precipitation and any snow falls in the watershed. Current land management practices within the watershed prohibit construction activities during this time. Further consideration should be given to the amount of sediments allowed to accumulate during the spring and summer seasons, and their placement in the watershed. The importance of the "relief" factor is that while soils may not be mobile during low or moderate precipitation storm events, they become mobile during intense storm events in the winter. The results of my study indicate that policies, practices and natural processes that limit sediment transport should be continued if not improved.

Future Work

I identified several areas for future work. While I was able to collect samples from soils in about 50% of the watershed, this only included five soil series. Additional samples from those five soil series might help reduce variance and increase the predictive capability of the phosphorus

models. Sampling from other soil series in the watershed might also help to increase the general predictive power of the models by considering more of the actual variation in soil properties within the watershed or it could just add more variation. Effort should be directed at increasing the resolution of soil series maps, accurately dating soil age, and connecting that to appropriate diagnostic data such as thorough assessments of geomorphology.

Conclusion

Soil bioavailable phosphorus was found to be 54% of soil TP_{pers} and approximately 600 times larger than soil SRP. A strong positive correlation was detected between BAP and TP_{pers}, indicating that one variable may be used to predict the other. A single factor linear model created to predict BAP as a function of TP_{pers} produced the most accurate estimates of BAP. No consistent relationships were identified between the soil parameters and soil series or size fractions. Correlation analysis identified weak but significant relationships between BAP and organic matter, slope and elevation. Slope and elevation were thought to influence sediment transport and erosion, while organic matter mediated soil phosphorus to dissolved phosphorus dynamics through mineralization and immobilization processes.

The theoretical link between TSS and TP_{pers} was used to estimate stream TP_{pers} and predict stream BAP, which was compared to estimated soil TP_{pers} and BAP. Predicted stream TP_{pers} from TSS was usually lower than measured stream TP_{pers}, but more closely matched measured TP_{pers} during periods of high stream discharge. These differences in stream phosphorus may be due to additional sources of phosphorus in the watershed or variations in soil phosphorus content.

Tables

Table 1. Forms of phosphorus theoretically accessed by the phosphorus extraction and digestion techniques used in my study are indicated by blue shading. Forms of phosphorus theoretically, but not empirically shown to be, accessed by a method are indicated with a "?".

SRP	$NaOH_{EDTA}$-P	Total persulfate phosphorus
soluble reactive	soluble reactive	soluble reactive
organic	organic	organic
sorbed	sorbed	sorbed ?
secondary inorganic	secondary inorganic	secondary inorganic ?
apatite	apatite	apatite

Table 2. Summary of physical properties for selected soil types in the Lake Whatcom watershed (NRCS, 2000, 2002a, 2000b, 2000c, 2004).

Soil Property	Soil series				
	Chuckanut	Sehome	Squalicum	Squires	Wickersham
Soil Order	Andisols	Andisols	Spodosols	Andisols	Inceptisols
Sub-order	Xerands	Xerands	Orthods	Xerands	Xerepts
Great Group	Vitrixerands	Vitrixerands	Haplorthods	Haploxerands	Dystroxerepts
Sub-group	Typic	Typic	Typic	Typic	Vitrandic
Family	Coarse-loamy, mixed, mesic	Coarse-loamy, mixed, mesic	Coarse-loamy, mixed, mesic	Loamy-skeletal, mixed, mesic	Coarse-loamy
Texture	Loam	Gravelly loam to loamy	Gravelly loam	Very channery loam	Channery silt loam
Particle Size	Ashy over loam	Medial	Coarse-loamy	Medial-skeletal	Coarse-loamy over sandy or sandy-skeletal
Soil Temperature	Mesic	Mesic	Mesic	Mesic	Mesic
Mineralogy	Amorphic, isotic	Mixed	Isotic	Amorphic	Mixed
Geologic Age	Eocene[2]	Jurassic[1] Eocene Pleistocene[3]	Eocene	Jurassic Pleistocene	Pleistocene Quaternary[4]
Lithology	Continental sedimentary deposits	Continental sedimentary deposits, continental glacial drift, low grade Phyllite	Continental sedimentary deposits	Low grade Phyllite, continental glacial drift	Continental glacial drift, mass wasting deposits
Geologic Notes	Chuckanut Formation	Chuckanut Formation, mostly Vashon Stade, Darrington Phyllite	Chuckanut Formation	Darrington Phyllite, mostly Vashon Stade	Mostly Vashon Stade

[1]199.6 to 145.5 million years ago; [2]55.8 to 33.9 million years ago; [3]2.588 million years ago to 12,000 years ago; [4]2.588 million years ago to present

Table 3. Soil series in the Lake Whatcom watershed, with area and percent coverage (Soil Conservation Service, 1992).

Soil Order	Soil Name	Area (m^2)	% Coverage
Alfisols		1,724,050	1.36
	Labounty	1,424,550	1.13
	Whitehorn	299,500	0.24
Andisols		45,557,854	36.02
	Barneston	1,594,120	1.26
	Chuckanut loam, bedrock substratum*	18,398,408	14.55
	Chuckanut-Urban land complex*	12,170	0.01
	Everett	640,000	0.51
	Getchell	3,687,180	2.92
	Montborne	1,890,450	1.49
	Sehome*	10,192,756	8.06
	Squires*	7,231,960	5.72
	Vanzandt	1,644,910	1.30
	Wollard	265,900	0.21
Andisols & Spodosols	Montborne-Rinker complex	3,261,086	2.58
Entisols	Kline	539,300	0.43
Histosols		760,571	0.60
	Histosols, ponded	22,270	0.02
	Pangborn	74,861	0.06
	Shalcar and Fishtrap soils	663,440	0.52
Inceptisols		2,029,650	1.60
	Bellingham	15,050	0.01
	Everett	337,000	0.27
	Wickersham*	1,337,600	1.06
	Winston	340,000	0.27
Inceptisols & Entisols	Briscot, Oridia, and Sumas soils	38,000	0.01
Mollisols	Puyallup	117,700	0.03

*samples collected from this soil series

Table 3 continued. Soil series in the Lake Whatcom watershed, with area and percent coverage.

Soil Order	Soil Name	Area (m^2)	% Coverage
Spodosols		50,355,346	39.81
	Comar	541,100	0.43
	Crinker-Rock outcrop complex	79,130	0.06
	Diobsud	9,599	0.01
	Everett	512,980	0.41
	Everett complex	1,312,050	1.04
	Nati	12,108,517	9.57
	Potchub	357,200	0.28
	Revel	5,362,040	4.24
	Revel-Welcome-Rock outcrop complex	3,506,000	2.77
	Rinker	133,350	0.11
	Springsteen	1,350,000	1.07
	Squalicum*	20,521,700	16.23
	Squalicum-Urban land complex*	2,678,500	2.12
	Typic Cryorthods	1,264,000	1.00
	Typic Cryorthods-Rock outcrop complex	127,980	0.10
	Whatcom	488,200	0.39
Spodosols & Alfisols	Whatcom-Labounty	181,709	0.14
	Andic Cryochrepts	1,175	0.00
	Andic Xerochrepts	1,525,670	1.21
	Andic Xerochrepts, cool-Rock outcrop complex	4,589,000	3.63
	Andic Xerochrepts-Rock outcrop complex	15,795,170	12.49
*samples collected from this soil series	TOTAL	126,476,281	99.92
	SAMPLED TOTAL	60,373,094	47.75

Table 4. Summary of Lake Whatcom watershed analytical methods and parameter abbreviations.

Abbreviation	Parameter	Units	Method
Phosphorus Analyses:			
srp	Soluble reactive phosphorus	µg P L^{-1} to mg P kg^{-1} soil	APHA (2005); H_2O extraction
bap	Bioavailable phosphorus*	µg P L^{-1} to mg P kg^{-1} soil	APHA (2005); NaOH + EDTA digestion
tp_{pers}	Total persulfate phosphorus	µg P L^{-1} to mg P kg^{-1} soil	APHA (2005); Persulfate digestion
Laboratory Analyses:			
om	Bulk organic matter	Percent (%)	NRCS (2010); Loss-on-ignition
ph	pH	pH units	APHA (2005)
psd	Particle size distribution	millimeters (mm)	Malvern (UK); Sandström *et al.* (2005)
sand	Sand	Percent by volume (%)	NRCS (2010)
silt	Silt	Percent by volume (%)	NRCS (2010)
clay	Clay	Percent by volume (%)	NRCS (2010)
Field measurements:			
aspect	Slope aspect	Degrees (°)	Compass
elevation	Meters above mean sea level	Meters (m)	Trimble (USA)
slope	Slope gradient	Percent (%)	Clinometer

Table 5. Correlation coefficients between BAP and water quality variables for all soil series (n = 195, p-value ≤ 0.05) and particle size, sand, silt and clay (n = 65, p-value ≤ 0.05). Non-significant correlations were omitted.

Kendall's τ	bap	srp	tp_{pers}	aspect	elevation	om	ph	slope	psd	sand	silt
srp	0.407***										
tp_{pers}	0.695***	0.440***									
aspect											
elevation	0.129**										
om	0.192***		0.111*		-0.141**						
ph				0.157**		-0.127**					
slope	0.173***	0.148**	0.162**		0.291***	-0.148**					
psd		0.202*	0.169*			0.233**					
sand						0.230**					
silt						-0.222**				-0.984***	
clay						-0.360***	0.260**			-0.726***	0.710***

* p-value< 0.05,**p-value < 0.01, *** p-value < 0.001

Kendall's τ	srp	tp_{pers}	aspect	elevation	om	ph	slope	psd	sand	silt	clay
bap	0.407***	0.695***		0.129**	0.192***		0.173***				

* p-value< 0.05,**p-value < 0.01, *** p-value < 0.001

Table 6. Comparison of soluble reactive, bioavailable, and total persulfate phosphorus concentrations in studies using the similar extraction techniques.

Source	Soil Source	SRP	BAP_{NaOH}	$TP_{persulfate}$	$TP_{persulfate}$: BAP_{NaOH}
		mg P kg $soil^{-1}$			
Liang (1994)	Whatcom, Nati, & Squalicum	0.3	330	630	1.9
		SRP	$BAP_{NaOH-EDTA}$	$TP_{persulfate}$	$TP_{persulfate}$: $BAP_{NaOH-EDTA}$
Groce (this study)	Median	0.6	356	664	1.9
	Chuckanut	0.5	412	630	1.5
	Sehome	0.4	320	619	1.9
	Squalicum	0.8	522	692	1.3
	Squires	1.0	559	959	1.7
	Wickersham	0.6	208	632	3.0

Table 6 continued. Comparison of soluble reactive, bioavailable, and total persulfate phosphorus concentrations in studies using the similar extraction techniques.

Source	Soil Source	SRP	BAP_{NaOH}	TP_{NaOH}	TP_{NaOH}: BAP_{NaOH}
		mg P kg soil^{-1}			
Turner & Engelbrecht (2011)	Minimum		18	43	2.4
	Median		81	185	2.3
	Maximum		330	824	2.5
Dou *et al.* (2009), untreated	Bucks		454	632	1.4
	Chester		453	730	1.6
	Duffield 1		289	468	1.6
	Glenelg		208	411	2.0
	Watson		243	621	2.6
Dou *et al.* (2009), manure treated	Duffield 2		1611	1800	1.1
	Hagerstown		1073	1298	1.2
	Manor		474	588	1.2
	Berks/Weikert 1		2740	2939	1.1
	Berks/Weikert 2		2616	2860	1.1
Zhang *et al.* (2009)	Lake Meiliang		1282	1362	1.1
	Lake Yuantouzhu		512	571	1.1
	Lake Gonghu		136	191	1.4
	Lake East Taihu		200	237	1.2
	Lake Hongfeng		363	482	1.3
	Lake Baihua		783	961	1.2
	Lake Erhai		326	474	1.5
Turner *et al.* (2003)	Minimum		44	73	1.7
	Median		124	210	1.7
	Maximum		200	323	1.6

Table 7. Principal components analysis results based on three variables (SRP, BAP and TP_{pers}) for the Lake Whatcom watershed soils data (n = 195, p-value ≤ 0.05).

Importance of components:			
	Comp1	Comp2	Comp3
Standard Deviation	1.54	0.76	0.24
Proportion of Variance	0.79	0.19	0.02
Cumulative Variance	0.79	0.98	1.00
Loadings:	Comp1	Comp2	Comp3
srp	-0.485	0.874	
tp_{pers}	-0.616	-0.363	-0.699
bap	-0.621	-0.322	0.715
Correlation:			
Kendall's τ	srp	tp	
tp_{pers}	0.440***		
bap	0.407***	0.695***	

*** p-value< 0.001

Table 8. Principal components analysis results based on eight variables (aspect, elevation, organic matter, pH, slope, SRP, BAP, and TP_{pers}) for the Lake Whatcom watershed soils data (n = 195, p-value ≤ 0.05). Additional components were omitted because of the minimal amount of variation explained by those components.

Importance of components:						
	Comp1	Comp2	Comp3	Comp4	Comp5	Comp6
Standard Deviation	1.59	1.20	1.07	0.98	0.87	0.74
Proportion of Variance	0.32	0.18	0.14	0.12	0.09	0.07
Cumulative Variance	0.32	0.50	0.64	0.76	0.86	0.93
Loadings:	Comp1	Comp2	Comp3	Comp4	Comp5	Comp6
aspect	-0.134	–	0.668	0.596	–	-0.401
elevation	-0.128	0.493	-0.259	0.618	–	0.534
om	–	-0.602	–	0.221	0.707	0.283
ph	-0.231	0.225	0.607	-0.421	0.166	0.542
slope	-0.215	0.508	-0.255	-0.167	0.618	-0.407
srp	-0.476	–	–	–	0.112	–
tp_{pers}	-0.567	-0.188	-0.131	–	-0.199	–
bap	-0.564	-0.224	-0.166	–	-0.185	–
Correlation:						
Kendall's τ	aspect	elevation	om	ph	slope	srp
elevation						
om		-0.141**				
ph	0.157**		–0.127**			
slope		0.291***	–0.148**			
srp					0.148**	
tp_{pers}			0.111*		0.162**	0.440***
bap		0.129**	0.192***		0.173***	0.407***

* p-value < 0.05 **p-value < 0.01 ***p-value < 0.001

Table 9. Principal components analysis results based on all variables (aspect, elevation, organic matter, pH, slope, particle size, sand, silt, clay, SRP, BAP, and TPP) for the Lake Whatcom watershed soils data as described in the "small" size fraction (n = 65, p-value ≤ 0.05). Additional components were omitted because of the minimal amount of variation explained by those components.

Importance of components:						
	Comp1	Comp2	Comp3	Comp4	Comp5	Comp6
Standard Deviation	1.88	1.63	1.12	1.08	0.96	0.95
Proportion of Variance	0.29	0.22	0.10	0.10	0.08	0.08
Cumulative Variance	0.29	0.52	0.62	0.72	0.79	0.87
Loadings:	Comp1	Comp2	Comp3	Comp4	Comp5	Comp6
aspect	-0.131	-0.103	0.372	–	-0.353	0.444
elevation	-0.159	-0.124	-0.465	-0.117	-0.649	0.361
om	0.309	-0.176	-0.139	0.454	0.185	–
ph	-0.223	–	0.568	-0.370	–	0.315
psd	0.127	-0.131	-0.341	-0.147	0.530	0.702
sand	0.492	–	0.133	-0.226	-0.211	–
silt	-0.487	–	-0.138	0.241	0.217	–
clay	-0.508	–	–	–	0.124	–
slope	-0.176	-0.290	-0.233	-0.384	-0.137	-0.183
srp	–	-0.447	0.303	-0.193	–	–
tp_{pers}	0.115	-0.552	–	0.143	–	–
bap	0.108	-0.224	-0.166	–	-0.185	–

Table 9 continued. Principal components analysis results based on all variables (aspect, elevation, organic matter, pH, slope, particle size, sand, silt, clay, SRP, BAP, and TPP) for the Lake Whatcom watershed soils data as described in the "small" size fraction (n = 65, p-value ≤ 0.05). Additional components were omitted because of the minimal amount of variation explained by those components.

Correlation:											
Kendall's τ	aspect	elevation	om	ph	psd	sand	silt	clay	slope	srp	tp_{pers}
elevation											
om		-0.141**									
ph	0.157**		-0.127**								
psd			0.233**								
sand			0.230**								
silt			-0.222**			-0.984***					
clay			-0.360***	0.260**		-0.726***	0.710***				
slope		0.291***	-0.148**								
srp					0.202*				0.148**		
tp_{pers}			0.111*		0.169*				0.162**	0.440***	
bap		0.129**	0.192***						0.173***	0.407***	0.695***

*p-value < 0.05 **p-value < 0.01 ***p-value < 0.001

Table 10. Predicted BAP as a function of measured TP_{pers} and SRP according to Equations 1 and 2, compared to measured BAP.

Equation 1: $\log_{10} \text{bap} = 1.39 \log_{10} \text{tp}_{\text{pers}} - 1.38$

	Measured TP_{pers} (mg P/kg soil)	Predicted BAP (mg P/kg soil)*	Measured BAP (mg P/kg soil)
Minimum	171	53 (45 – 63)	54
Median	664	354 (333 – 377)	359
Maximum	3648	3793 (3192 – 4506)	4001

* 95% confidence intervals

Equation 2: $\log_{10} \text{bap} = 0.55 \log_{10}(\text{tp}_{\text{pers}} + \text{srp}) + 1.13$

	Measured TP_{pers} (mg P/kg soil)	Predicted BAP (mg P/kg soil)*	Measured BAP (mg P/kg soil)
Minimum	171	44 (34 – 57)	54
Median	664	363 (334 – 394)	359
Maximum	3648	3972 (3053 – 5168)	4001

* 95% confidence intervals

Table 11. Predicted BAP and TP_{pers} as a function of total suspended sediments (TSS) concentrations collected from the Silver Beach Creek, where TSS was assumed to represent soil inputs to Lake Whatcom from the Silver Beach Creek sub-watershed. Measured stream TP_{pers} (Stream TP_{pers}) concentrations were used in Equation 1 to generate predicted stream BAP (Pred. Stream BAP) concentrations, while TP_{pers} predicted from TSS values (TSS Pred. TP_{pers}) concentrations were used in Equation 1 to generate TSS predicted BAP concentrations (TSS Pred. BAP).

Date	Time	Flow (cfs)	Stream TSS* mg L^{-1}	Stream TP_{pers}* µg P L^{-1}	TSS Pred. TP_{pers} µg P L^{-1}	% Diff TPP	Pred. Stream BAP µg P L^{-1}	TSS Pred. BAP µg P L^{-1}	% Diff BAP
11/16	14:57	2.7	6.8	29.4	4.5	-85	4.6	0.3	-93
11/16	18:09	6.9	49.1	64.2	32.6	-49	13.6	5.3	-61
11/16	19:57	9.6	113.3	115.3	75.3	-35	30.6	16.9	-45
11/16	21:25	10.1	84.4	94.1	56.1	-40	23.1	11.6	-50
11/16	23:01	8.6	42.5	79.9	28.2	-65	18.4	4.3	-77
11/17	12:58	7.7	24.4	51.7	16.2	-69	10.0	2.0	-80
11/17	3:03	8.6	70.2	89.2	46.6	-48	21.4	8.7	-59
11/17	4:01	18.6	258.0	178.9	171.4	-4	56.4	53.1	-6
11/17	4:53	16.7	92.3	117.8	61.4	-48	31.5	12.8	-59
11/17	5:43	21.6	239.1	200.8	158.9	-21	66.2	47.8	-28
11/17	6:21	24.6	229.9	171.5	152.8	-11	53.2	45.3	-15
11/17	6:58	23.2	164.1	158.3	109.1	-31	47.6	28.4	-40
11/17	7:42	19.1	123.5	163.2	82.1	-50	49.6	19.1	-61
11/17	8:36	16.1	85.6	97.4	56.9	-42	24.2	11.5	-52
11/17	9:37	14.3	49.9	63.4	33.1	-48	13.3	5.4	-59
11/17	10:46	13.1	42.7	65.5	28.4	-57	14.0	4.4	-69
11/17	13:09	10.7	35.9	70.6	23.9	-66	15.5	3.4	-78
11/17	16:01	9.1	17.5	41.6	11.6	-72	7.4	1.3	-82
11/17	19:14	8.9	29.6	47.9	19.7	-59	18.1	2.6	-86
11/17	21:07	20.2	73.7	93.7	49.0	-48	22.9	9.3	-59
11/17	22:40	16.0	42.7	79.9	28.4	-64	18.4	4.4	-76
11/18	12:41	12.4	23.0	49.2	15.3	-69	9.4	1.9	-80
11/18	3:07	10.9	17.6	48.0	11.7	-76	9.1	1.3	-86
11/18	5:47	10.2	14.1	41.4	9.4	-77	7.4	0.9	-88

*(R. Matthews, personal communication, 11/24/2010)

$$\text{Pred. stream } TP_{pers} = \frac{\text{TSS mg}}{\text{L}} \times \frac{\text{kg soil}}{10^6 \text{ mg soil}} \times \frac{\text{median mg } TP_{pers}}{\text{kg soil}} \times \frac{10^3 \text{ µg } TP_{pers}}{\text{mg } TP_{pers}} = \frac{\text{µg } TP_{pers}}{\text{L}}$$

Equation 1. $\log_{10} bap = 1.39 \log_{10} tp_{pers} - 1.38$

Figures

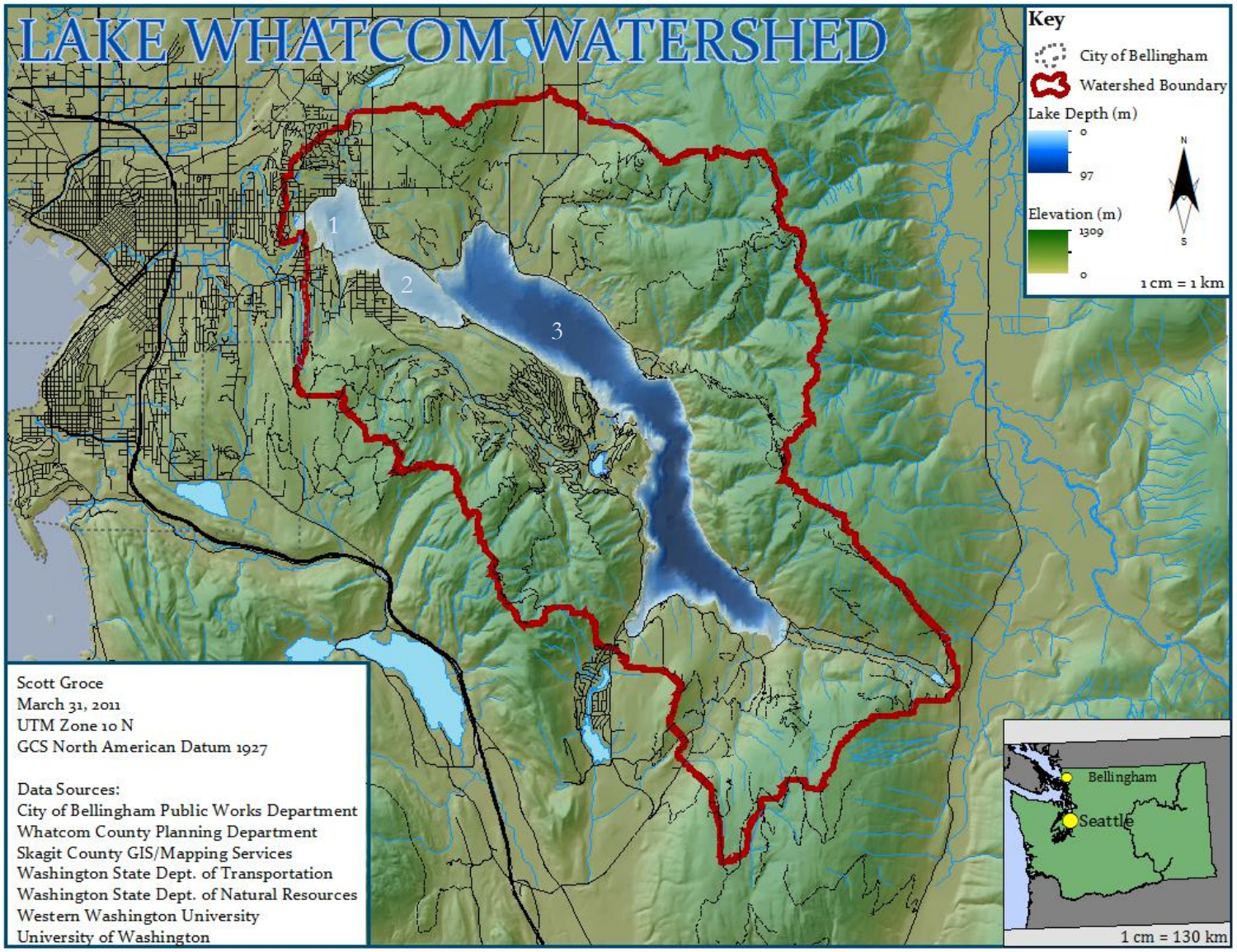

Figure 1. The Lake Whatcom watershed, City of Bellingham and surrounding areas.

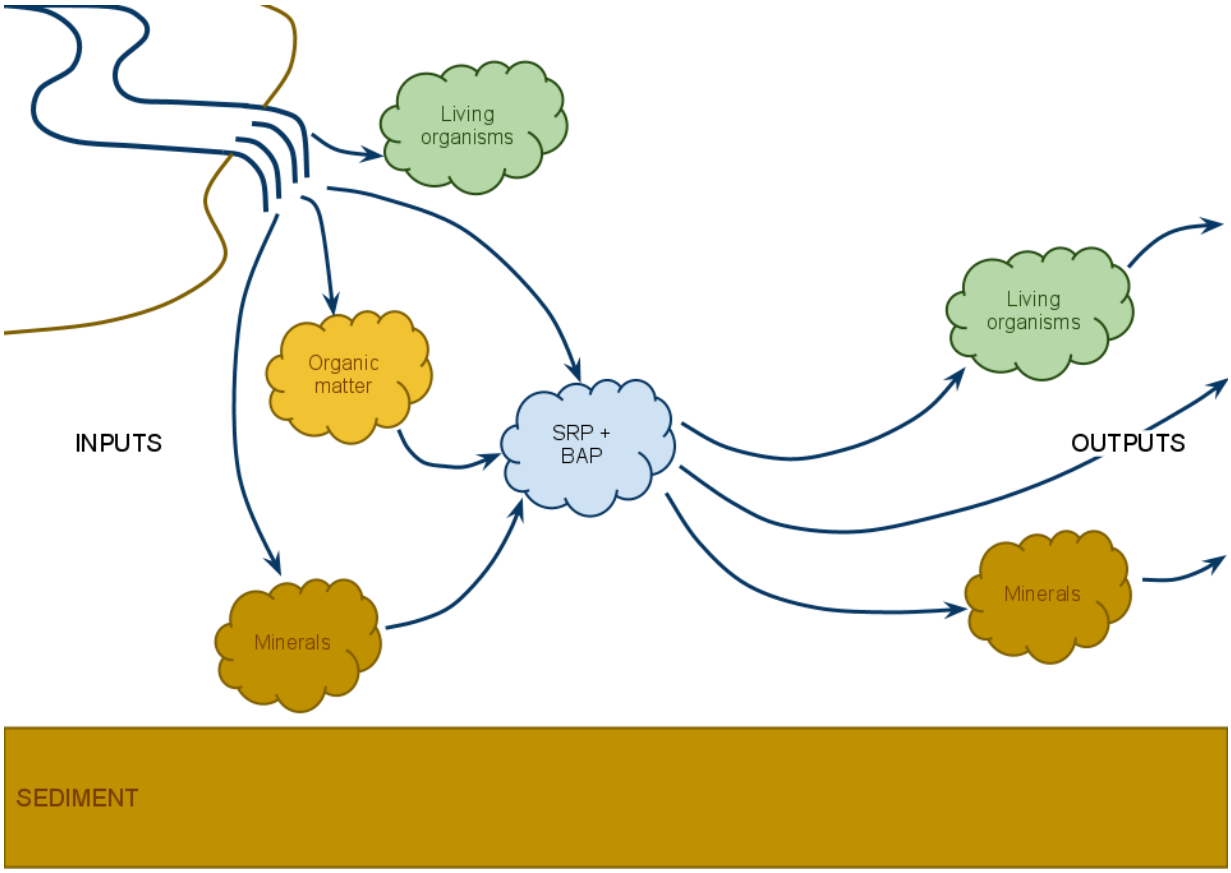

Figure 2. A freshwater phosphorus cycle showing simplified relationships between inputs and outputs (adapted from Cavaliere, 2010).

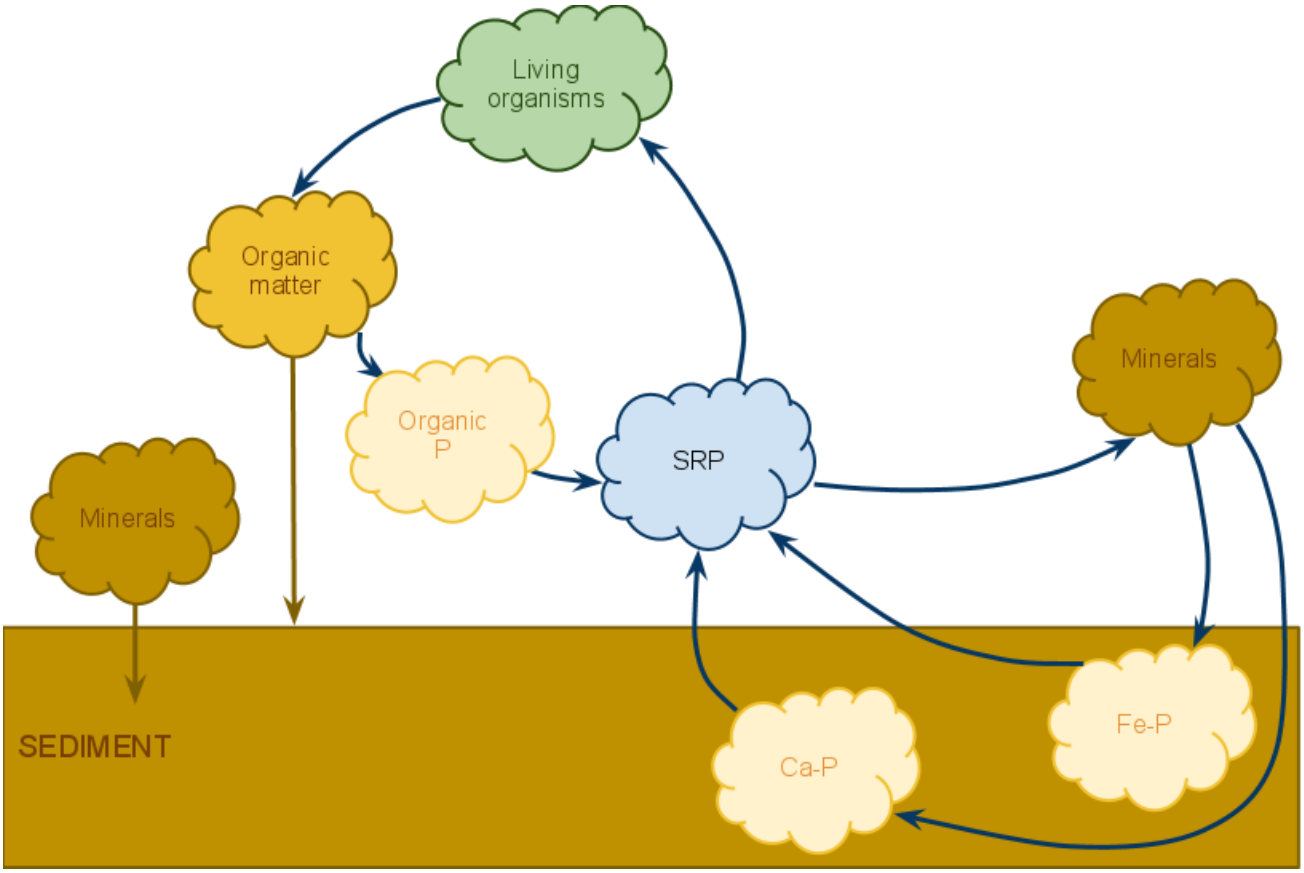

Figure 3. Phosphorus cycling between organic and inorganic forms in freshwater. Deposition and burial of organic matter and mineral particulates is also shown (adapted from Cavaliere, 2010).

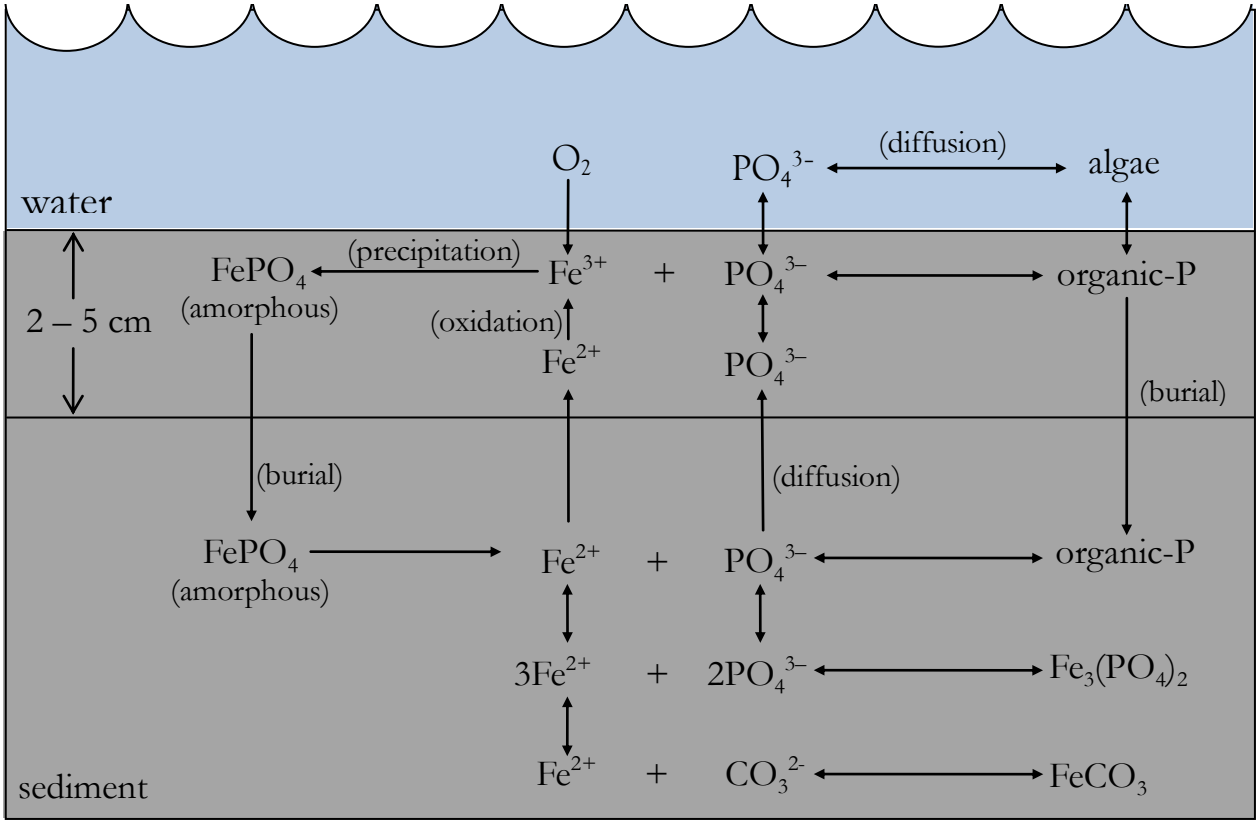

Figure 4. Phosphorus exchange dynamics at the freshwater/sediment interface (adapted from Wetzel, 2001).

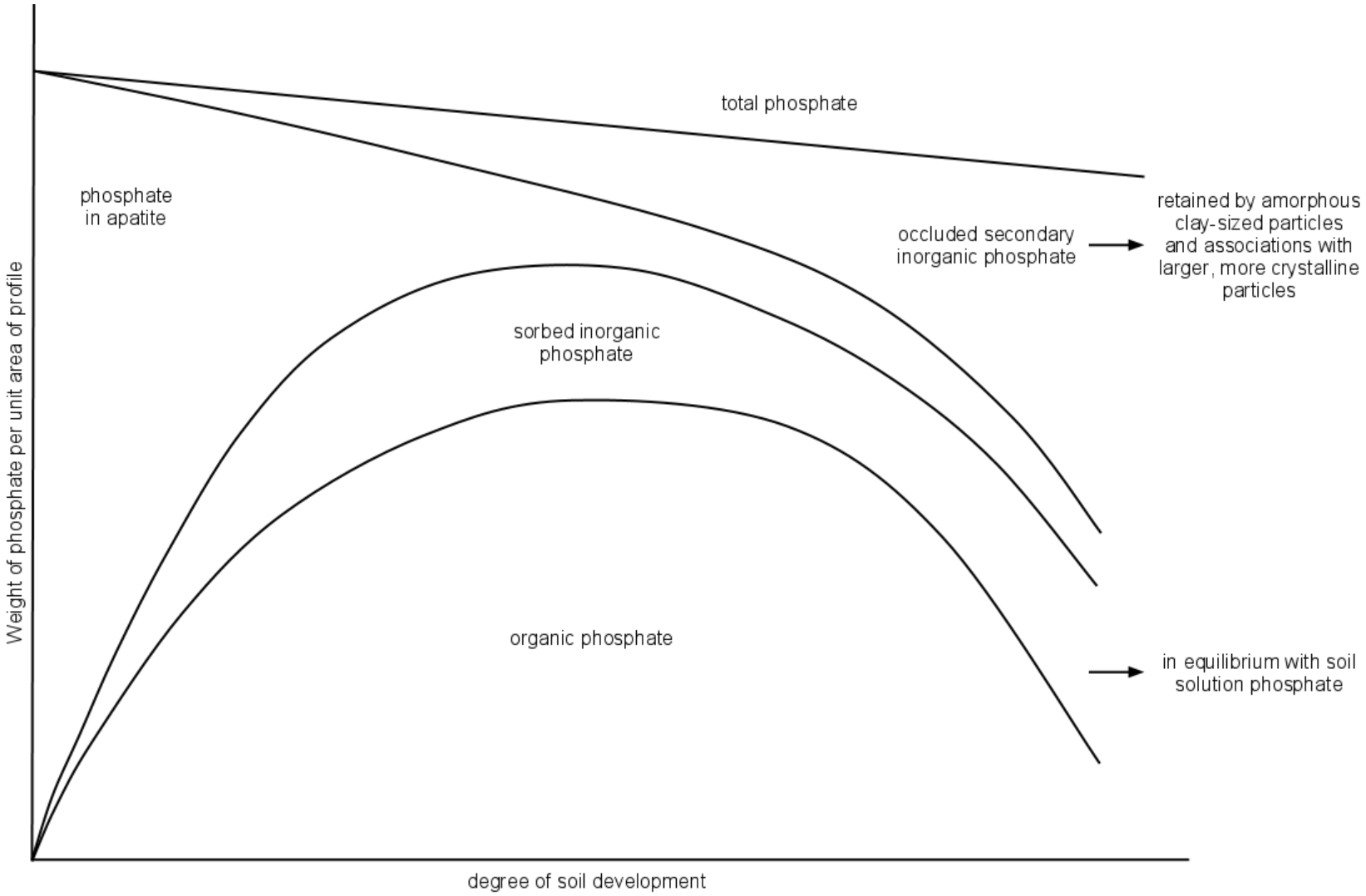

Figure 5. Changes in the proportion of amount of phosphate per unit area of soil profile as the degree of soil development increases (adapted from Williams and Walker, 1969).

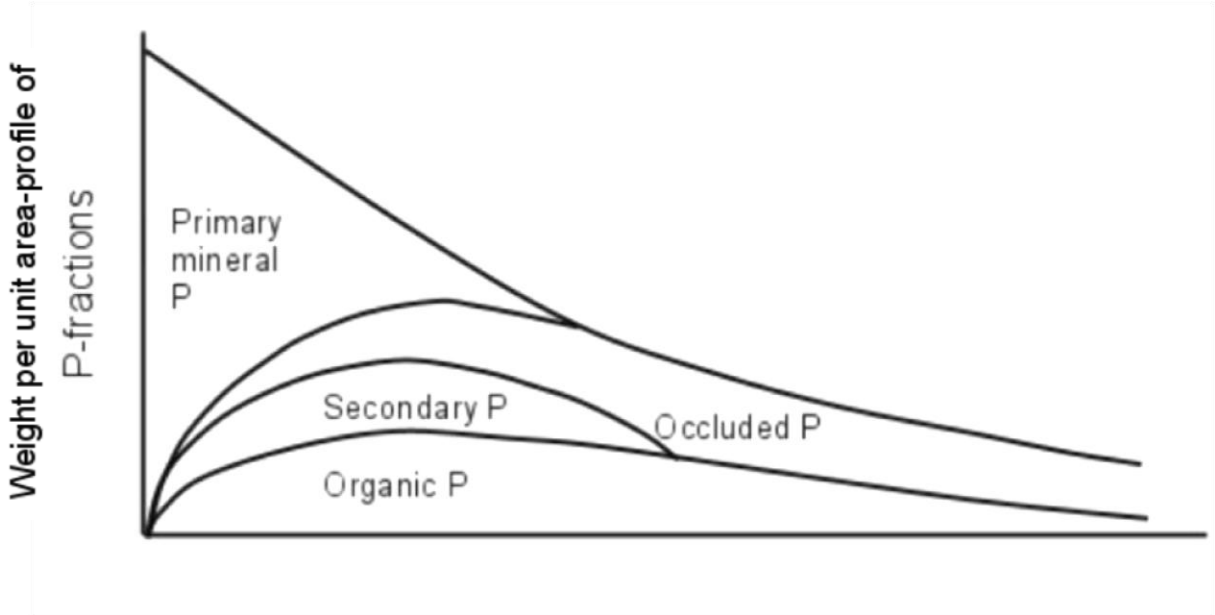

Figure 6. Temporal changes in form of soil phosphorus (Stewart & Tiessen, 1987; adapted from Walker and Syers, 1976).

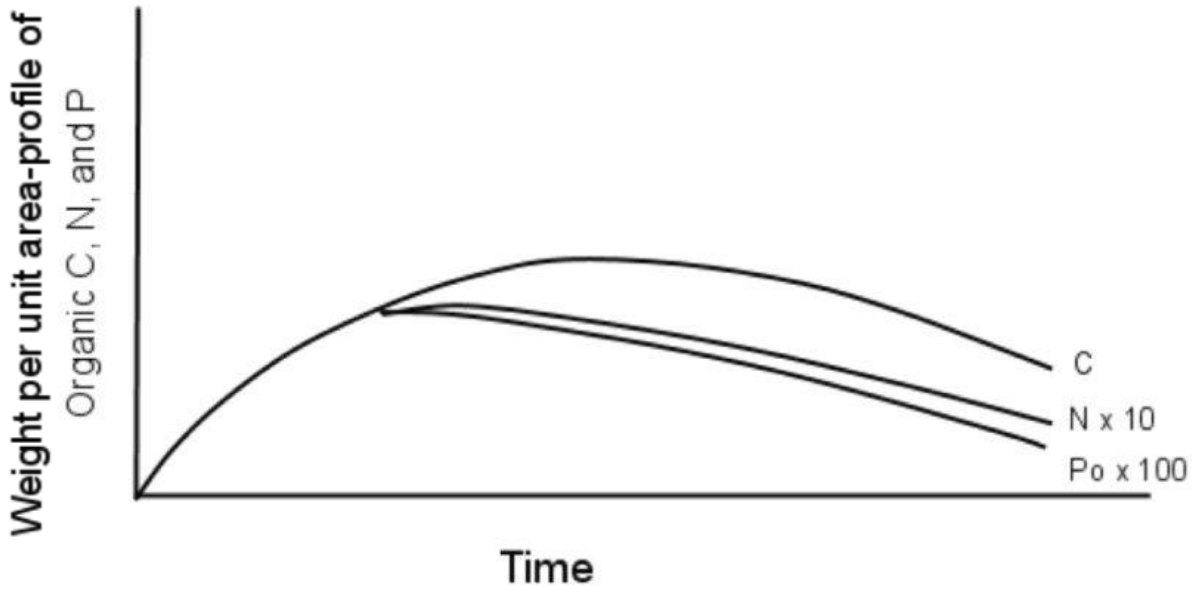

Figure 7. Temporal changes in amounts of soil phosphorus and soil organic constituents (Stewart & Tiessen, 1987; adapted from Floate, 1971).

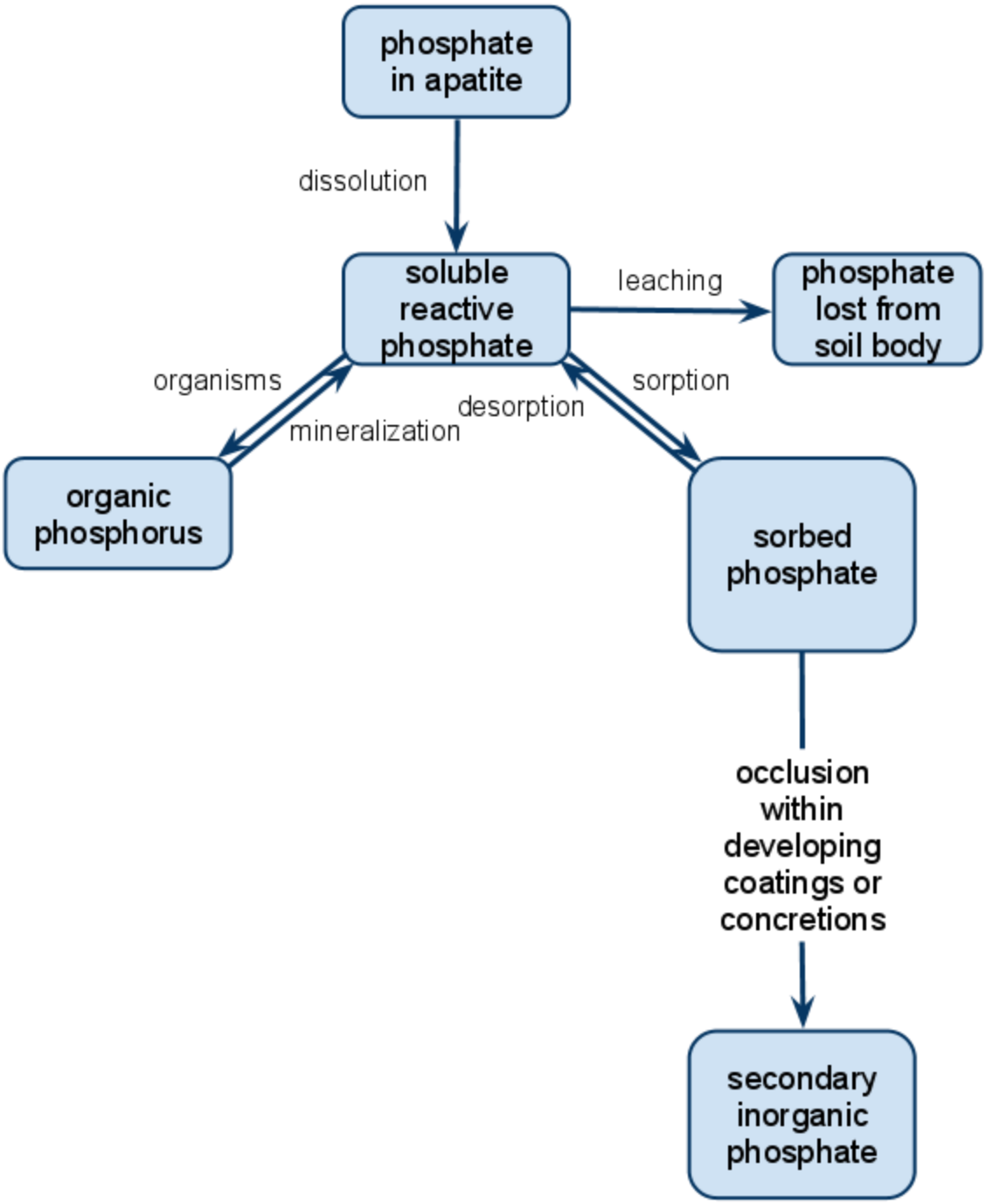

Figure 8. Phosphate transformations in acid soils during pedogenesis (adapted from Williams and Walker, 1969).

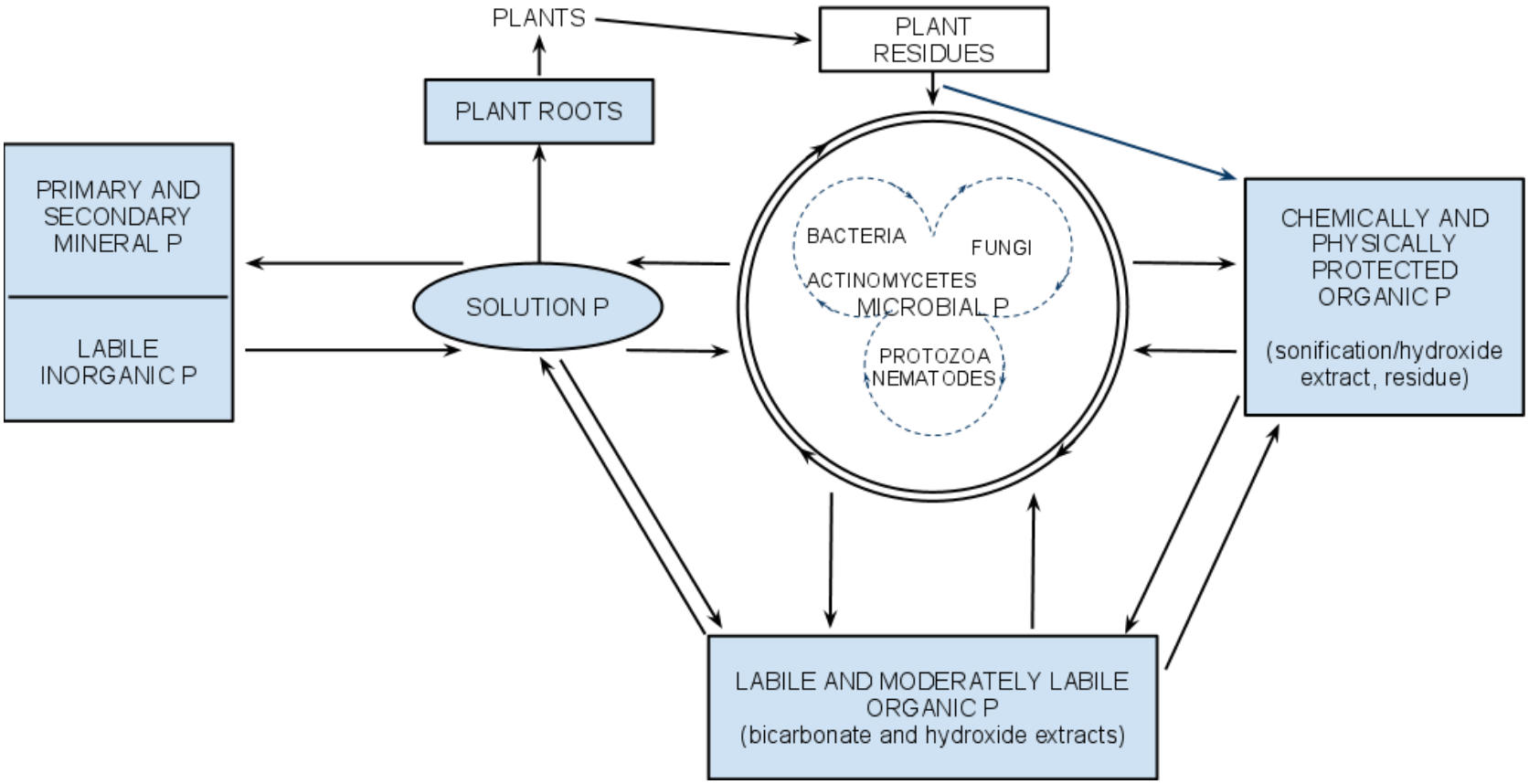

Figure 9. Soil phosphorus cycling processes and common analytical methods used to access identified phosphorus fractions (adapted from Stewart and Tiessen, 1987).

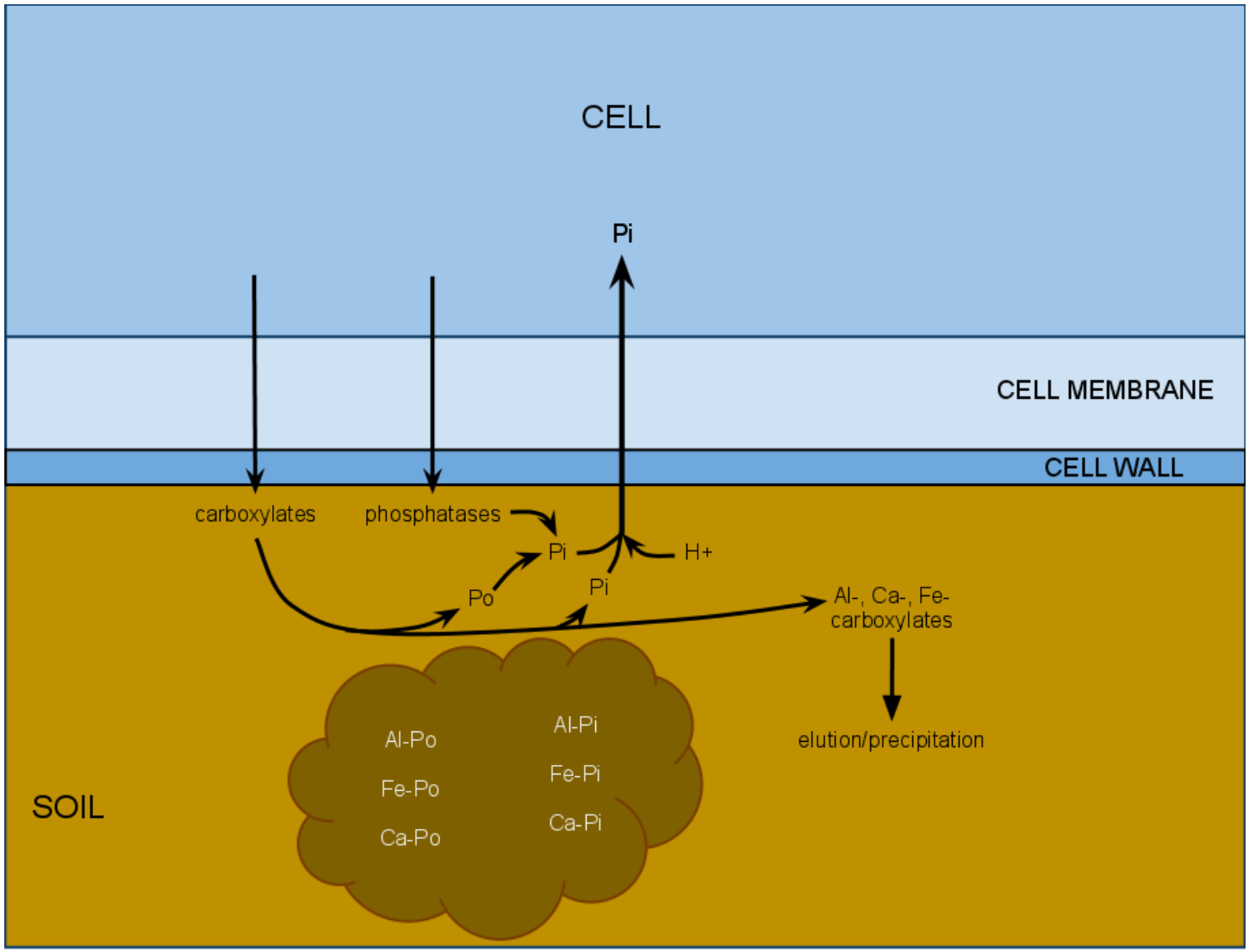

Figure 10. Phosphorus solubilization and transport mechanisms used by heterotrophs to increase phosphorus availability (adapted from Lambers *et al.*, 2008).

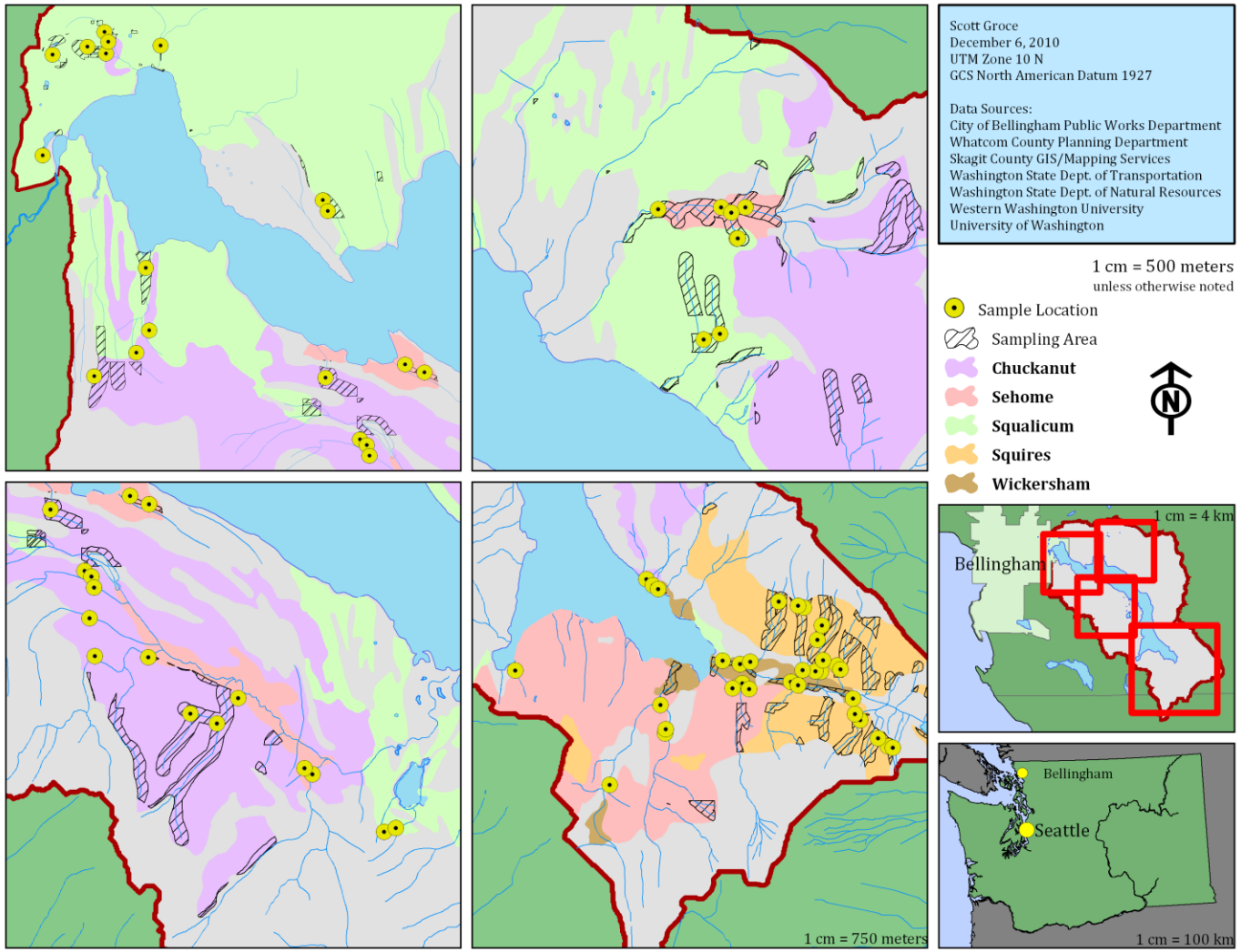

Figure 11. Soil series and sample locations within the Lake Whatcom watershed. Sampling buffers created to select sample locations from while in the field. Buffers were created using the following criteria: within the NRCS mapped area of a desired soil series, ¼ mile from a road, 150 feet from a stream, and on publicly owned land.

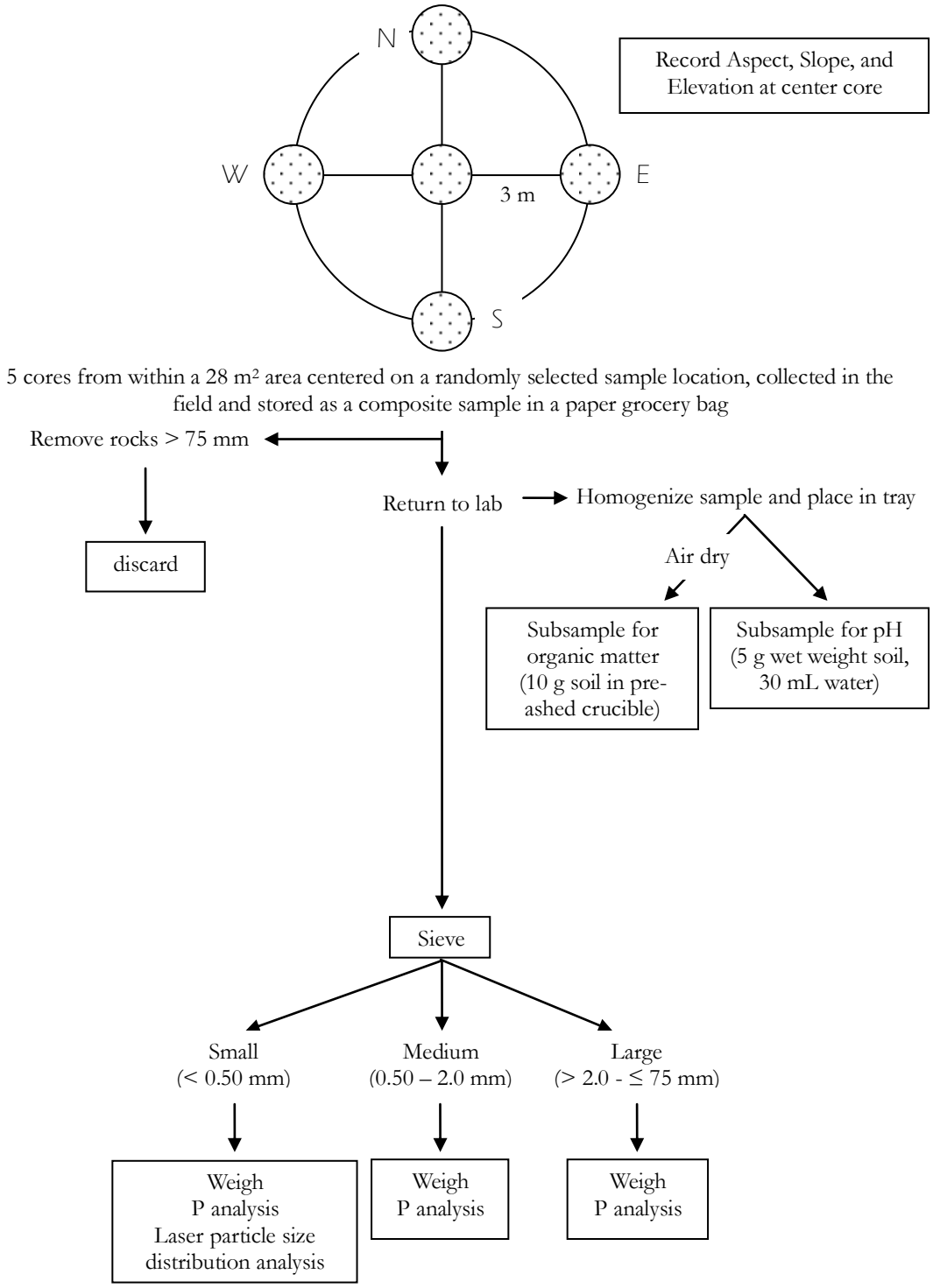

Figure 12. Soil sample treatment procedures used to measure variables in the Lake Whatcom watershed (adapted from Sandström, 2005).

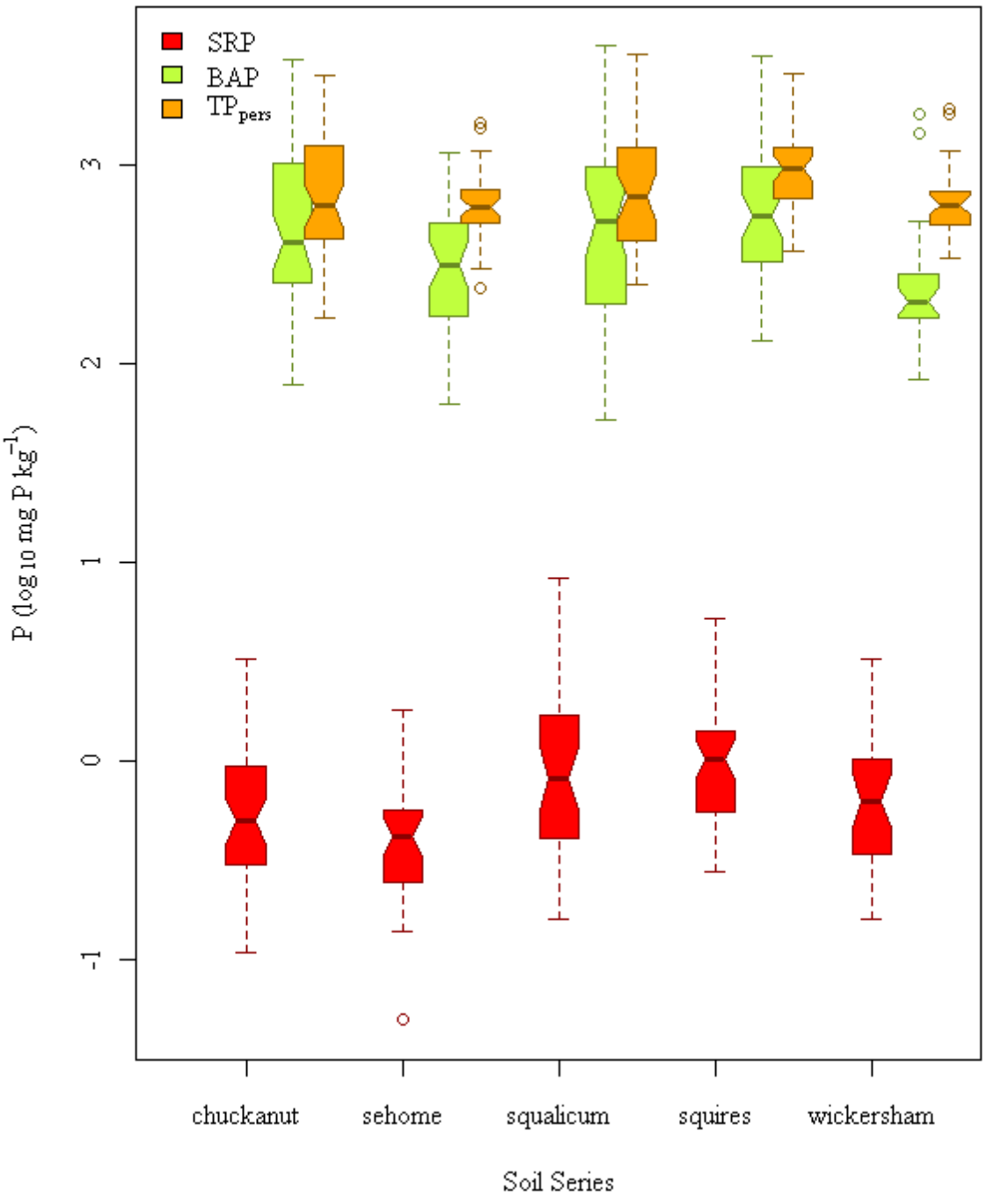

Figure 13. Boxplots showing relationships between SRP, BAP, and TP_{pers} concentration in sampled soil series from the Lake Whatcom watershed. Overlapping notches show pairs that are not significantly different (Dalgaard, 2002).

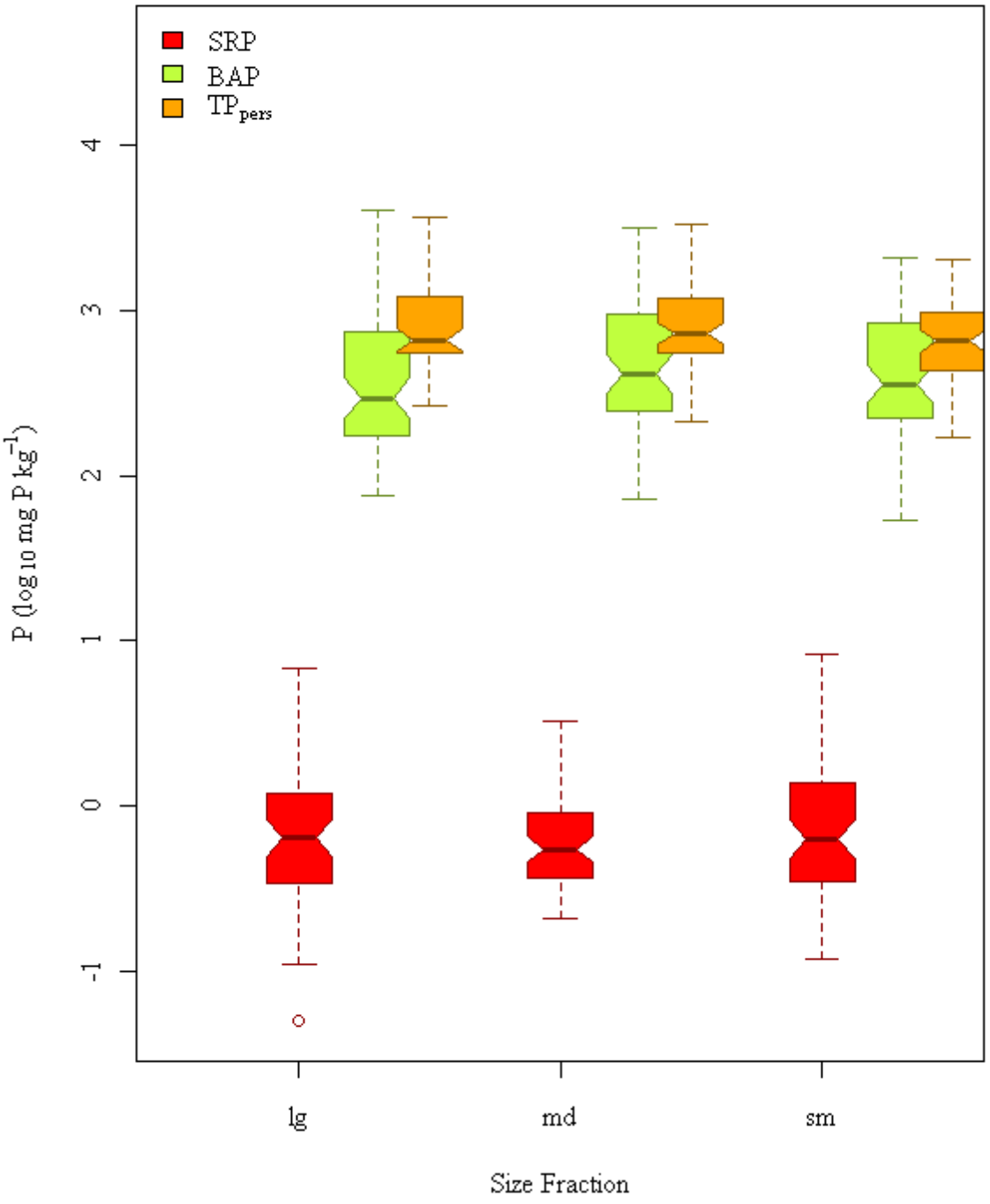

Figure 14. Boxplots showing relationships between SRP, BAP, and TP_{pers} concentration and size fraction in soil samples from the Lake Whatcom watershed. Overlapping notches show pairs that are not significantly different (Dalgaard, 2002).

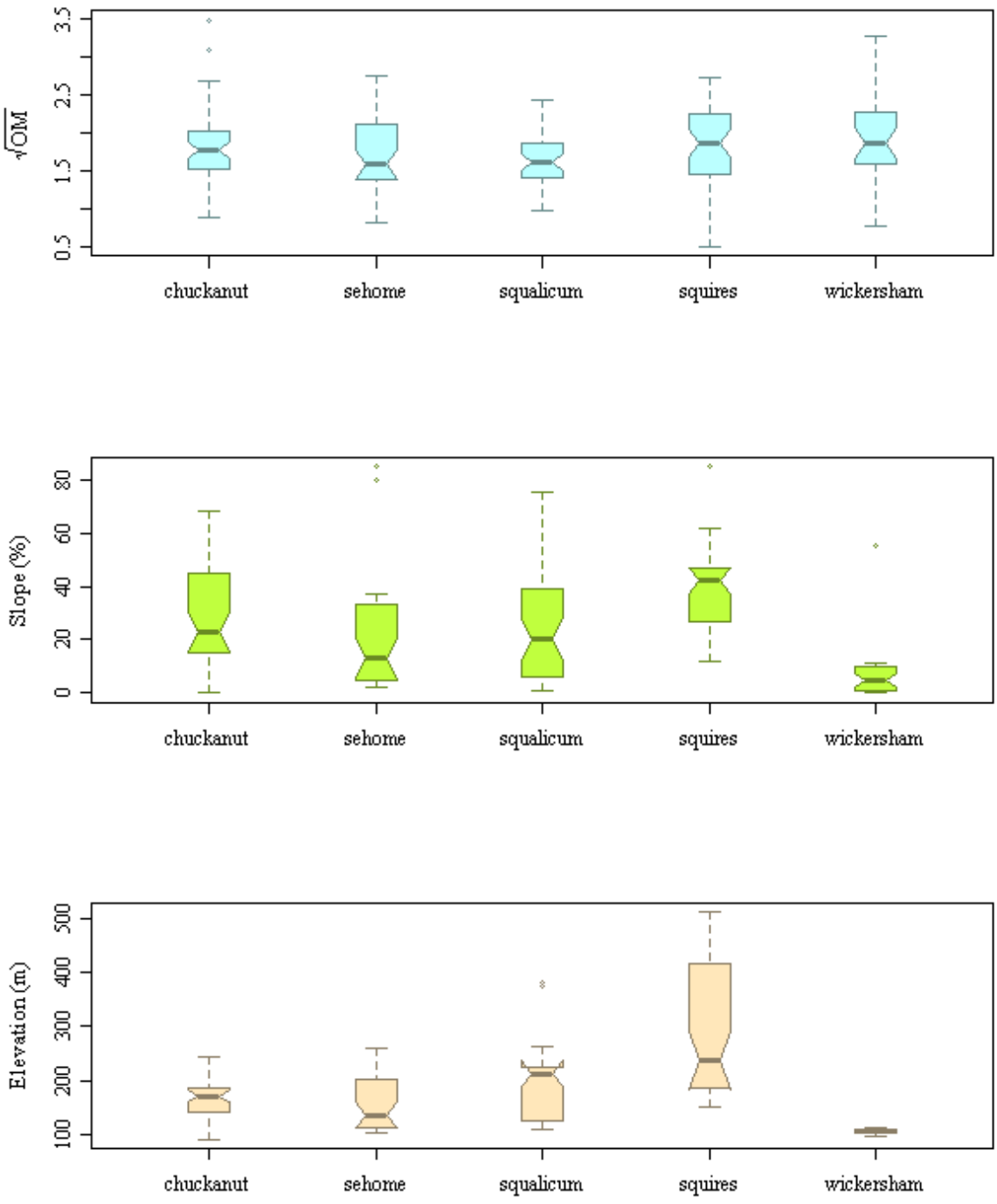

Figure 15. Boxplots showing relationships between organic matter, slope and elevation in sampled soil series from the Lake Whatcom watershed. Overlapping notches show pairs that are not significantly different (Dalgaard, 2002).

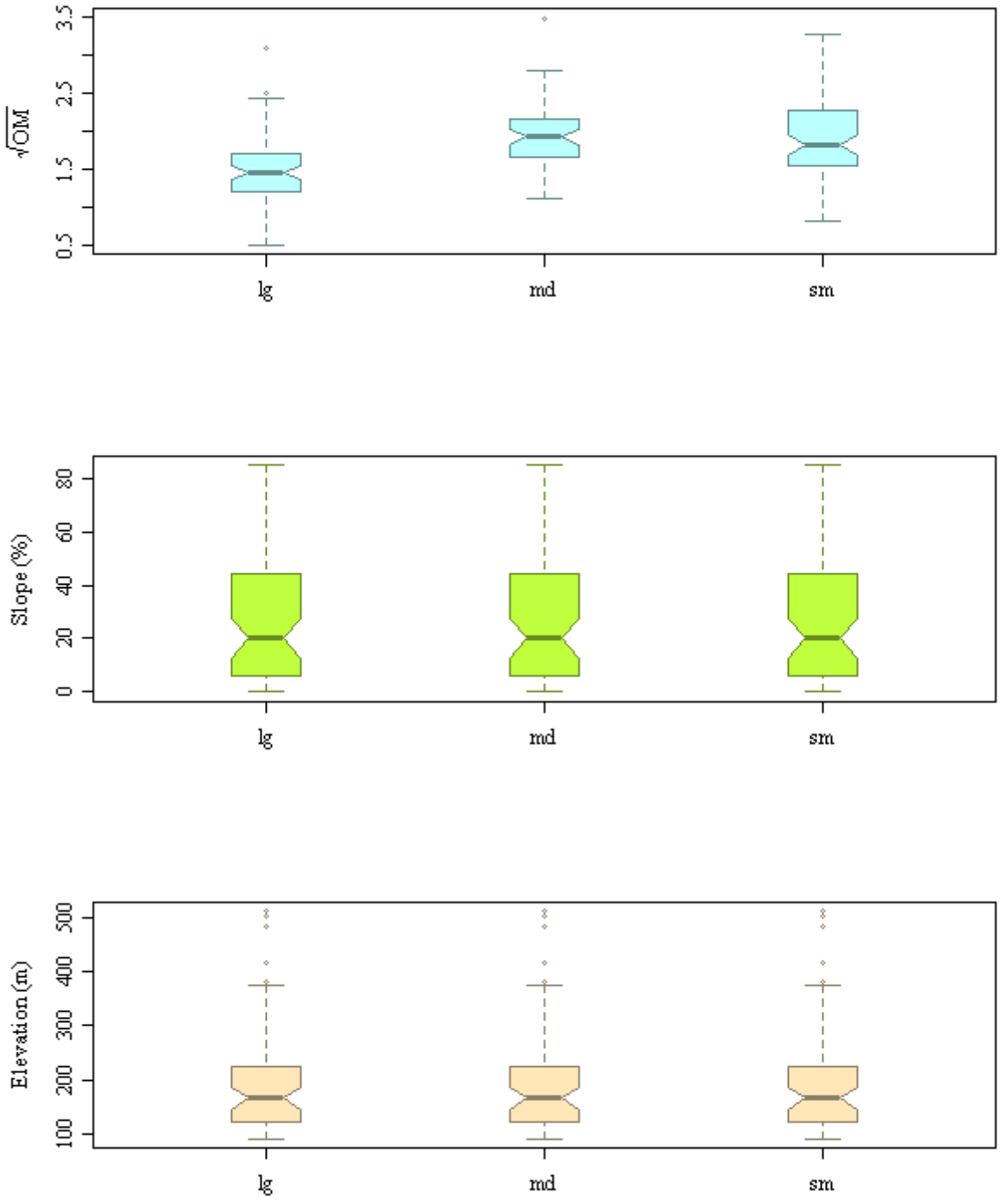

Figure 16. Boxplots showing relationships in organic matter, slope and elevation between size fractions in soils samples from the Lake Whatcom watershed. Overlapping notches show pairs that are not significantly different (Dalgaard, 2002).

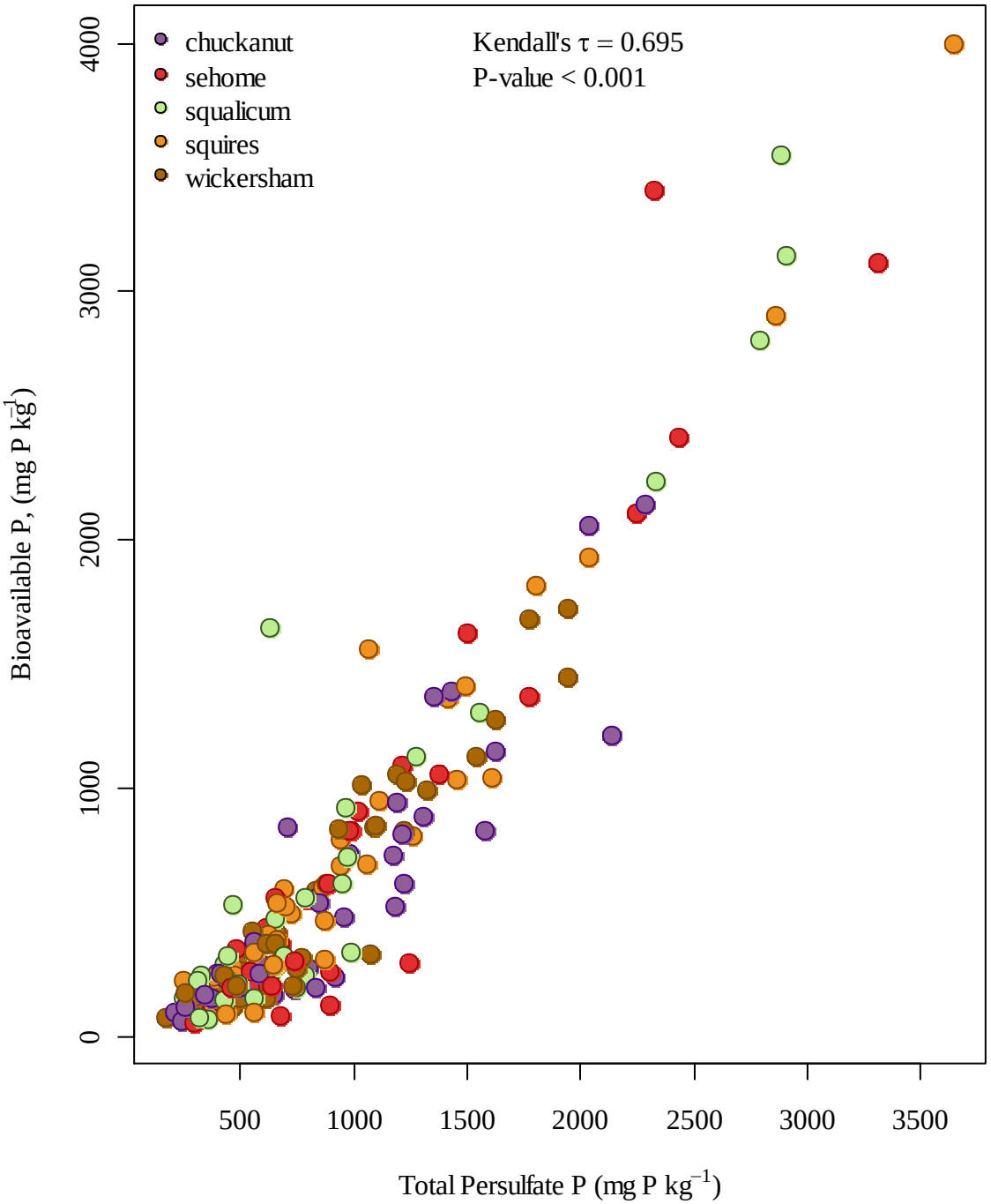

Figure 17. Association between BAP and TP_{pers} in soil samples from the Lake Whatcom watershed.

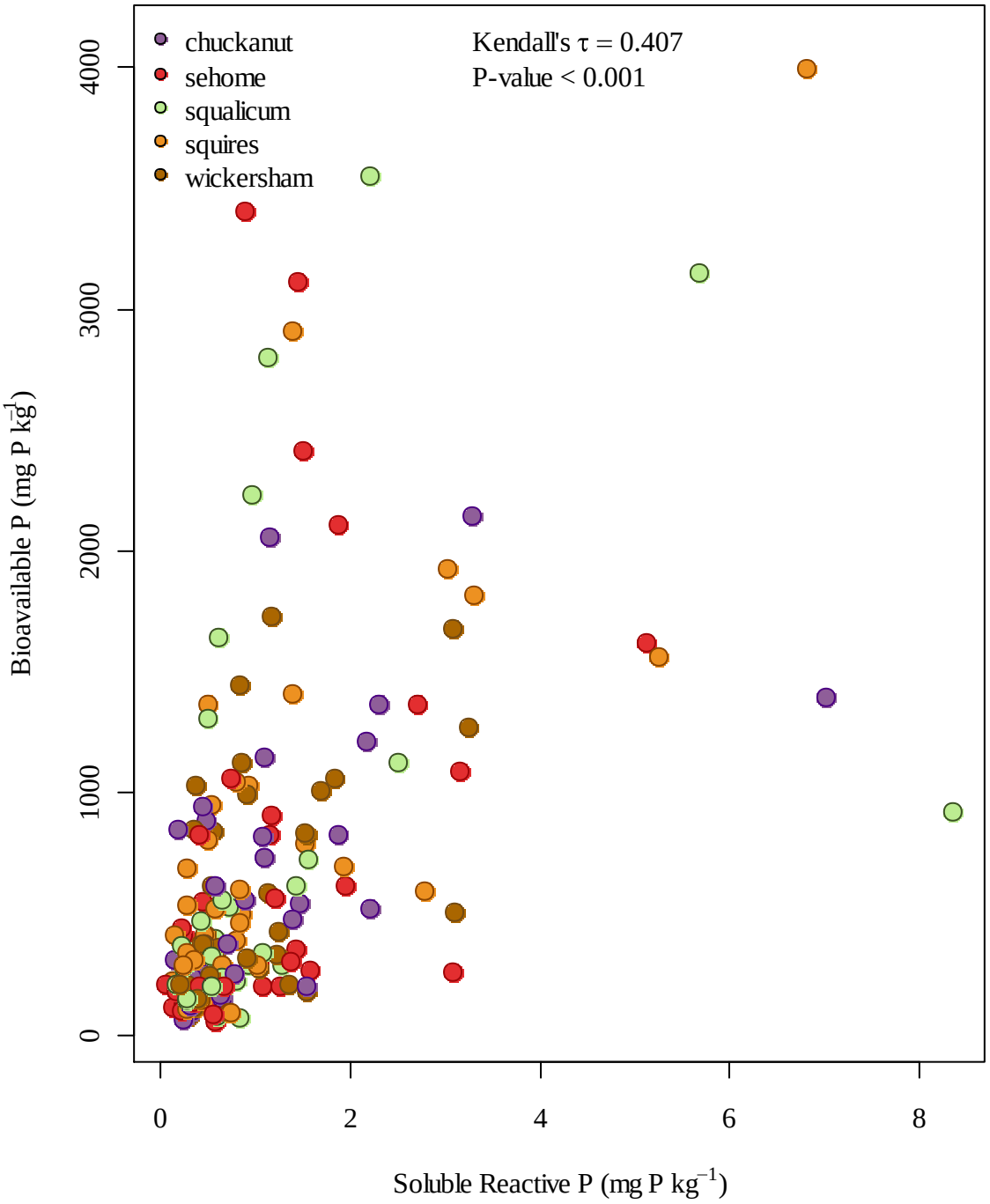

Figure 18. Association between BAP and SRP in soil samples from the Lake Whatcom watershed.

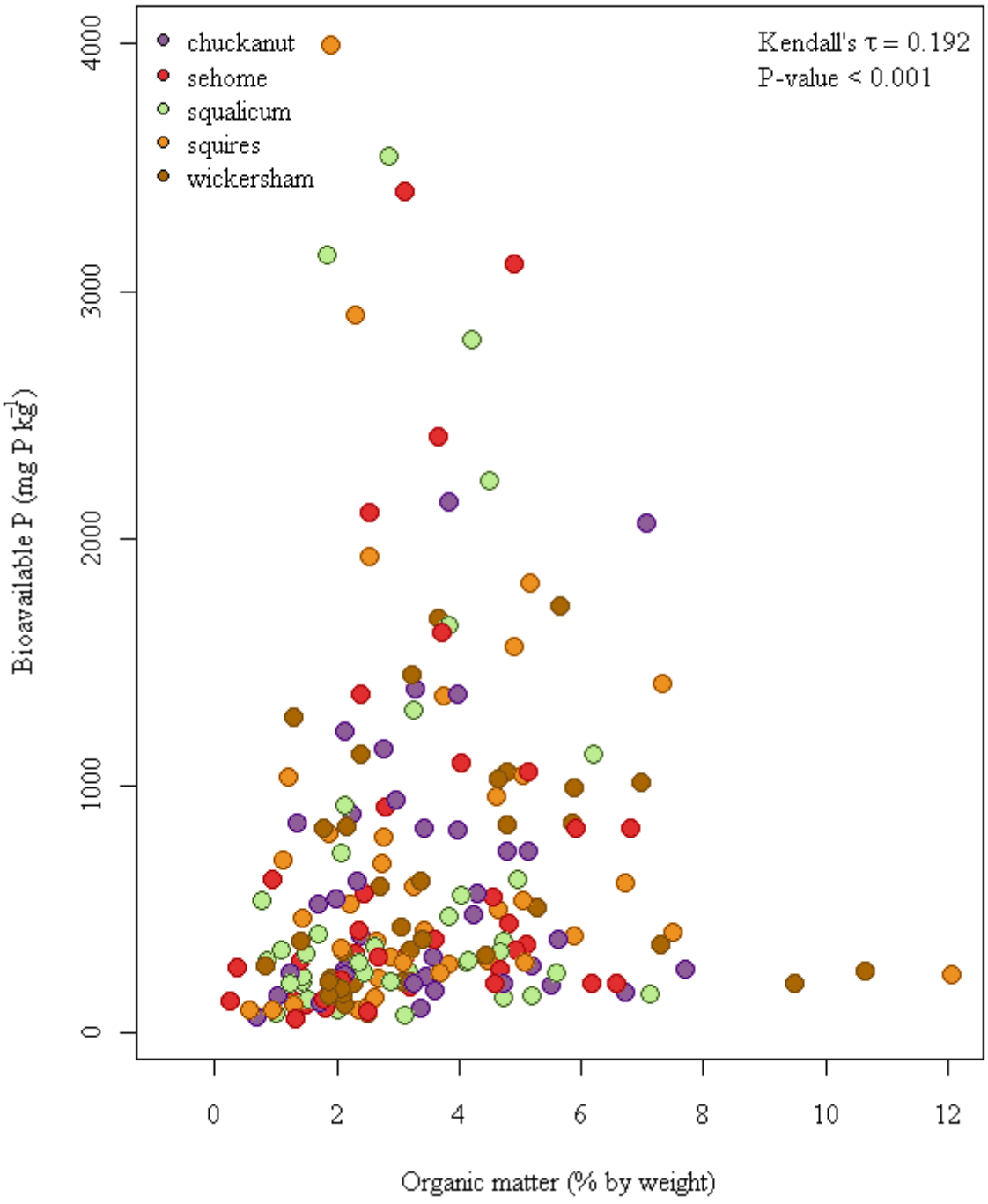

Figure 19. Association between BAP and organic matter in soil samples from the Lake Whatcom watershed.

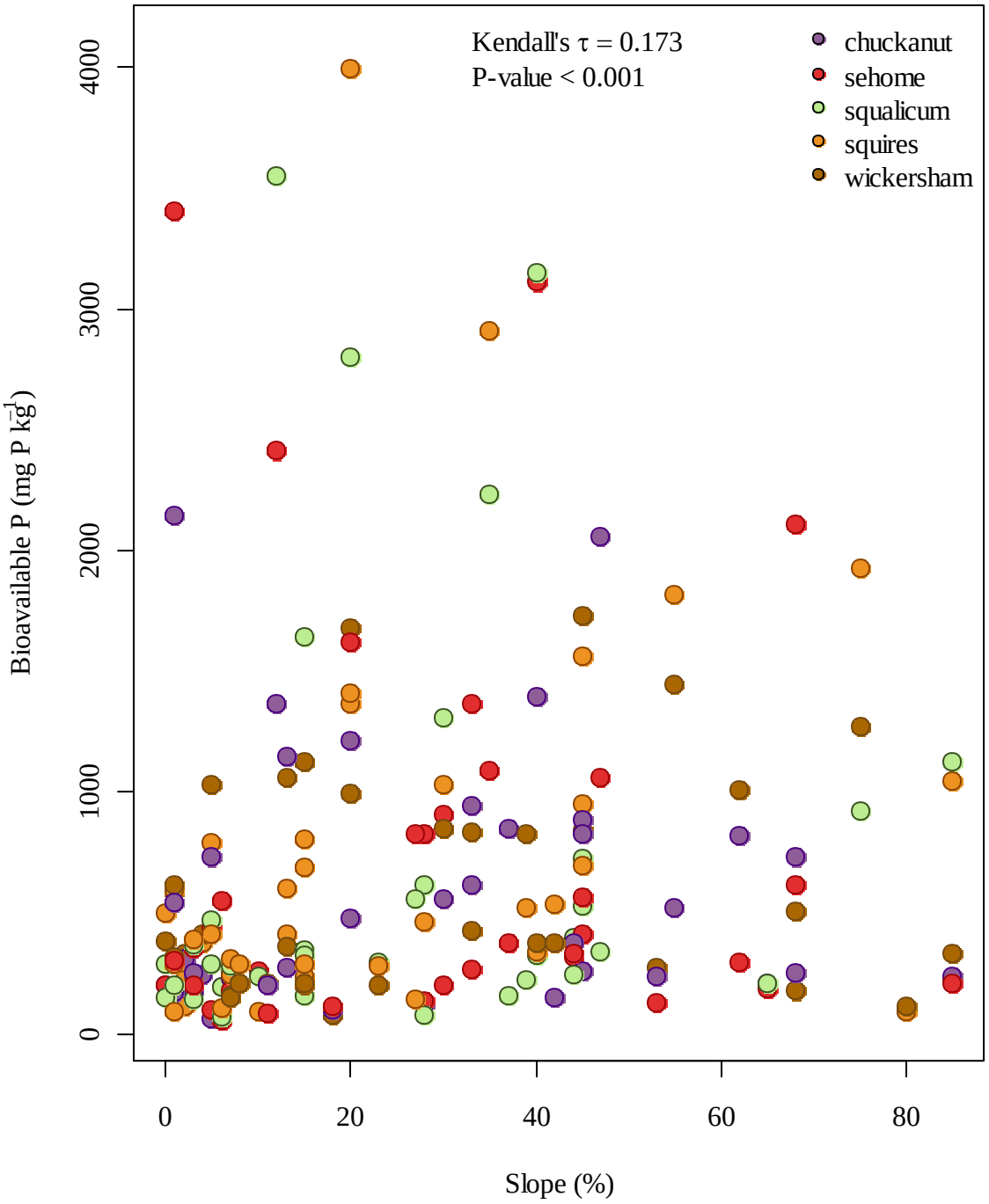

Figure 20. Association between BAP and slope in soil samples from the Lake Whatcom watershed.

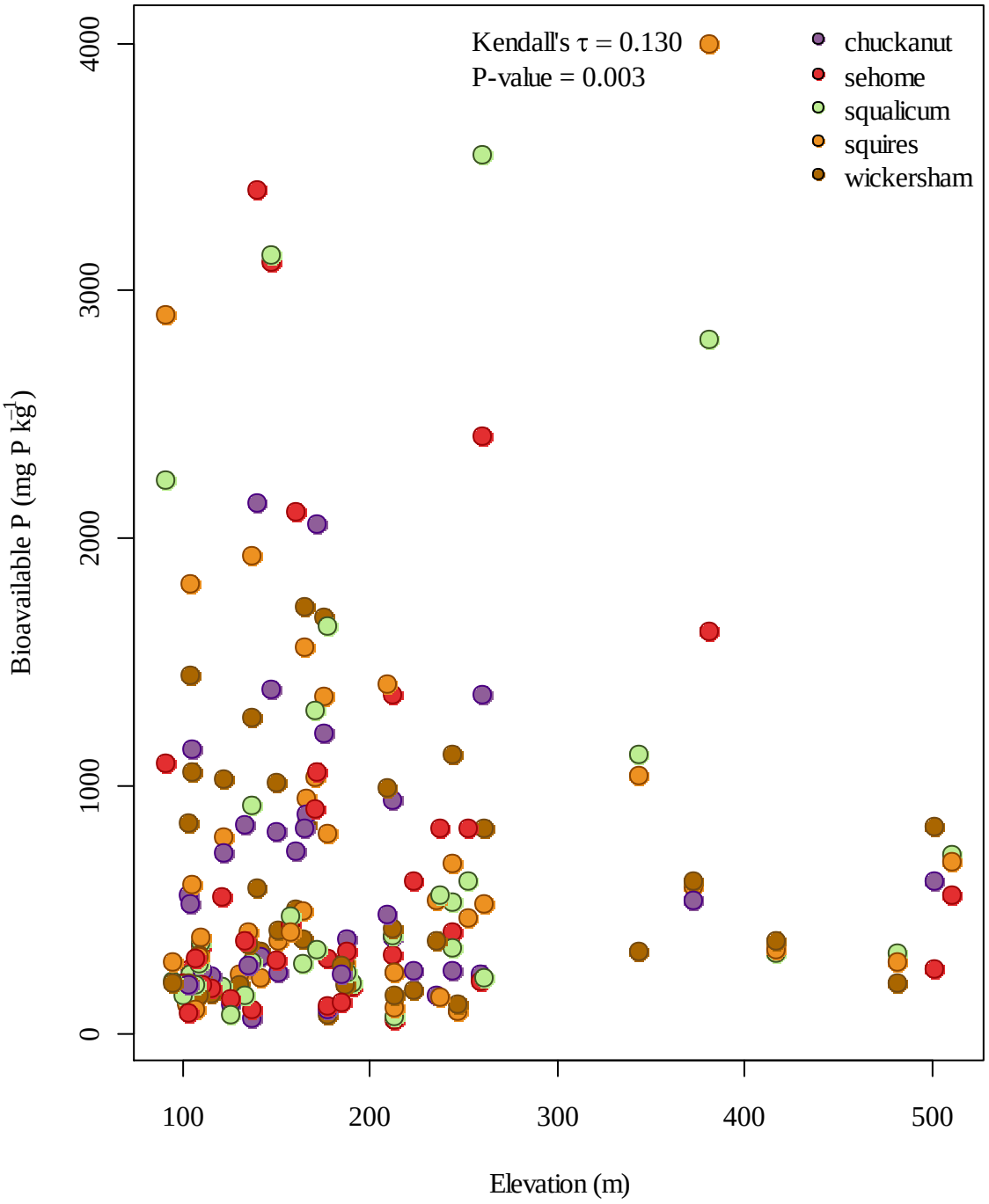

Figure 21. Association between BAP and elevation in soil samples from the Lake Whatcom watershed.

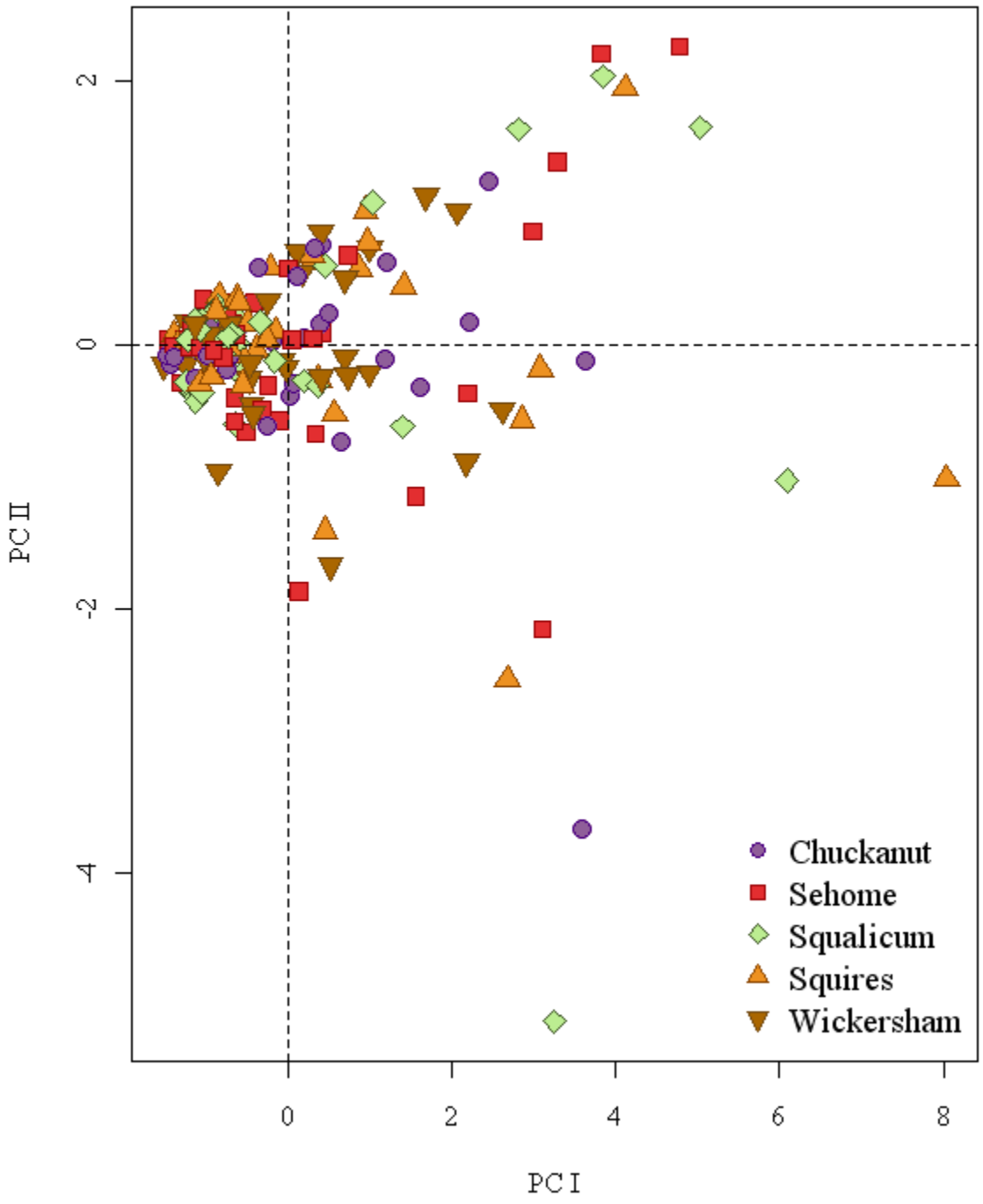

Figure 22. Principal components ordination based on SRP, BAP, and TP_{pers} showing soil series.

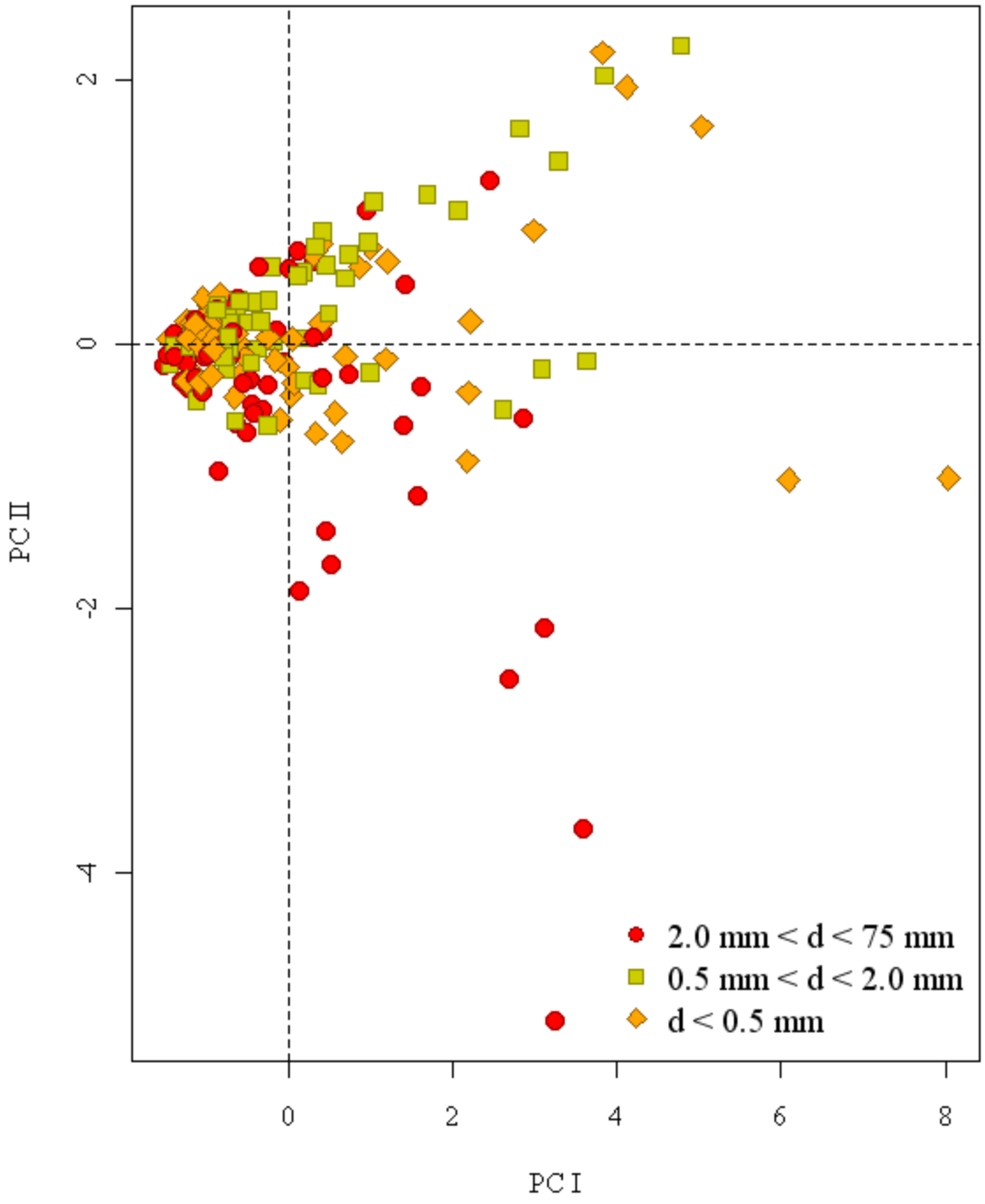

Figure 23. Principal components ordination based on SRP, BAP, and TP_{pers} showing size fraction.

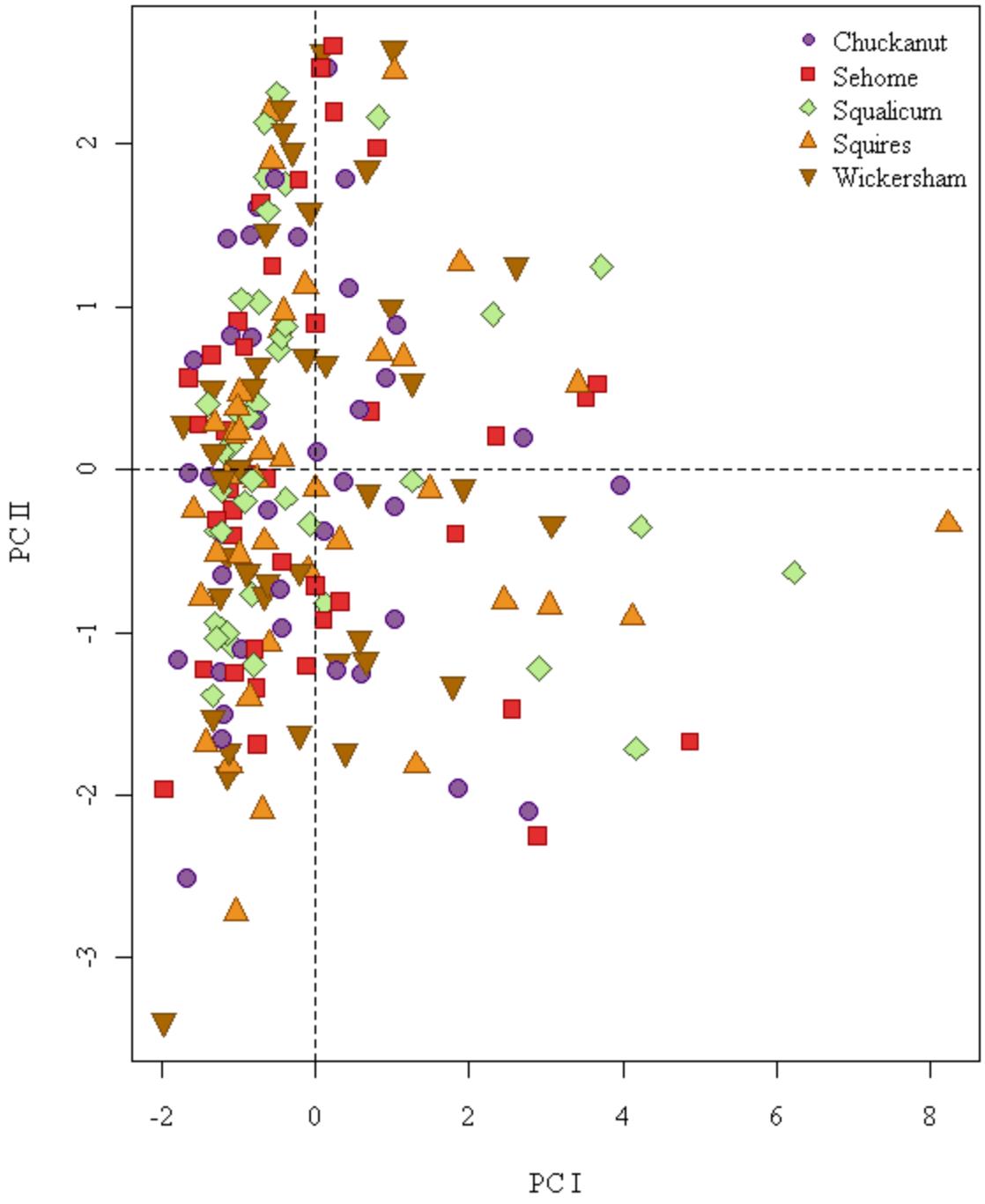

Figure 24. Principal components ordination based on aspect, elevation, organic matter, slope, SRP, BAP and TP_{pers} showing soil series.

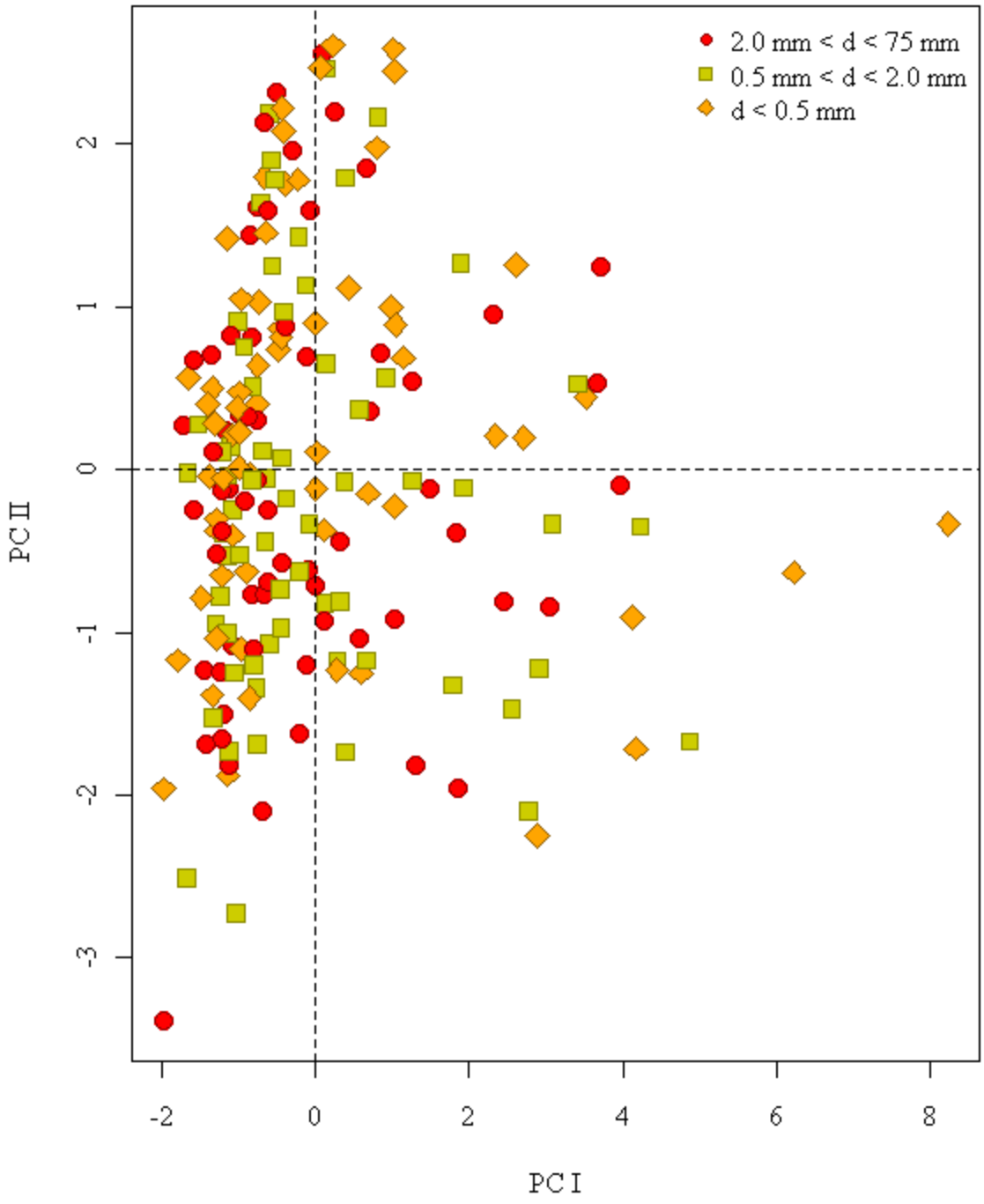

Figure 25. Principal components ordination based on aspect, elevation, organic matter, slope, SRP, BAP and TP_{pers} showing size fraction.

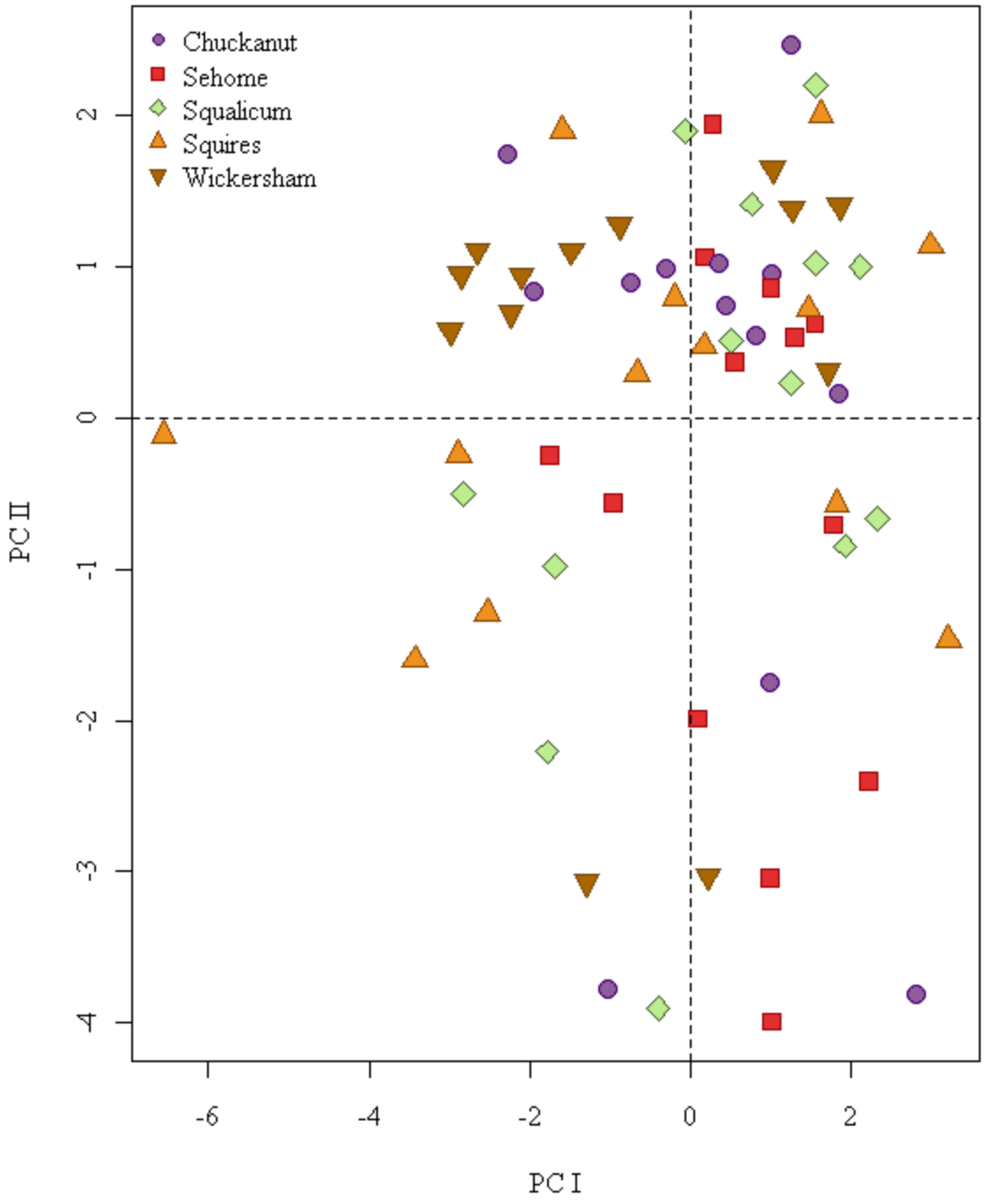

Figure 26. Principal components ordination based on aspect, elevation, organic matter, pH, slope, SRP, BAP, TP_{pers}, particle size, sand, silt and clay within the "small" size fraction showing soil series.

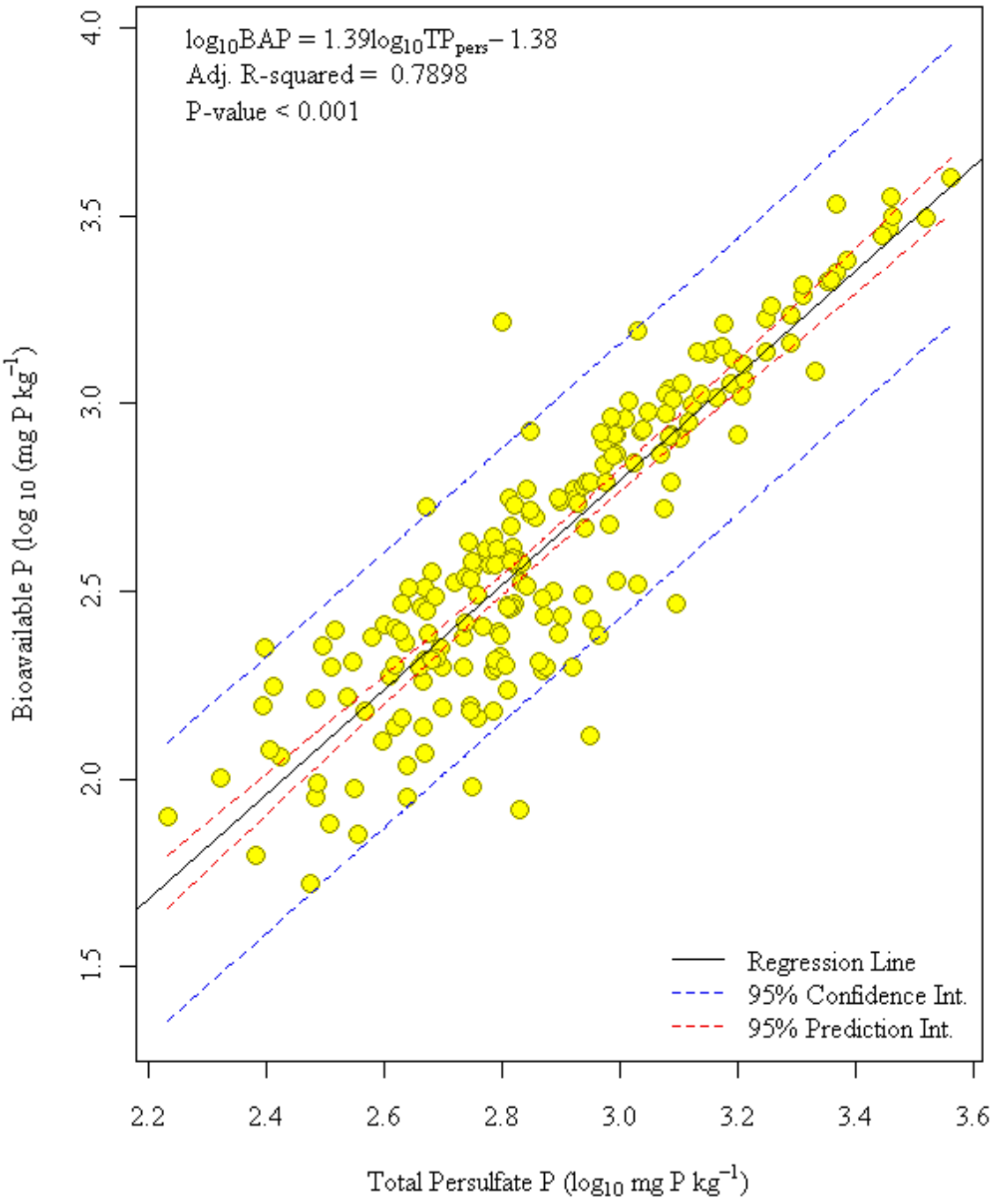

Figure 27. Linear regression model of BAP as a function of TP_{pers} (Equation 1). Red lines indicate 95% confidence intervals; blue lines indicate 95% prediction intervals.

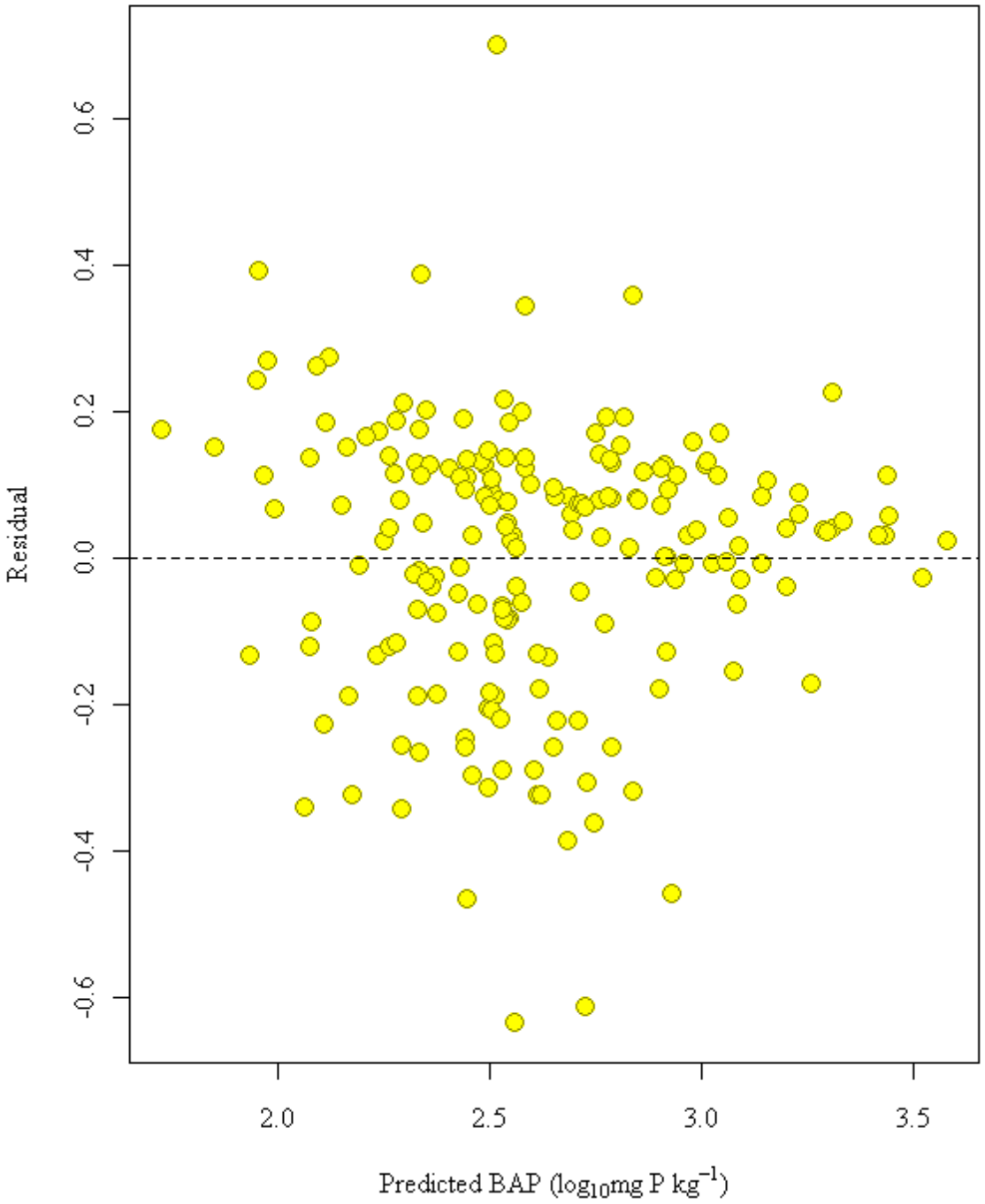

Figure 28. Linear regression model residuals for bivariate linear model predicting BAP as a function of TP_{pers} (Equation 1).

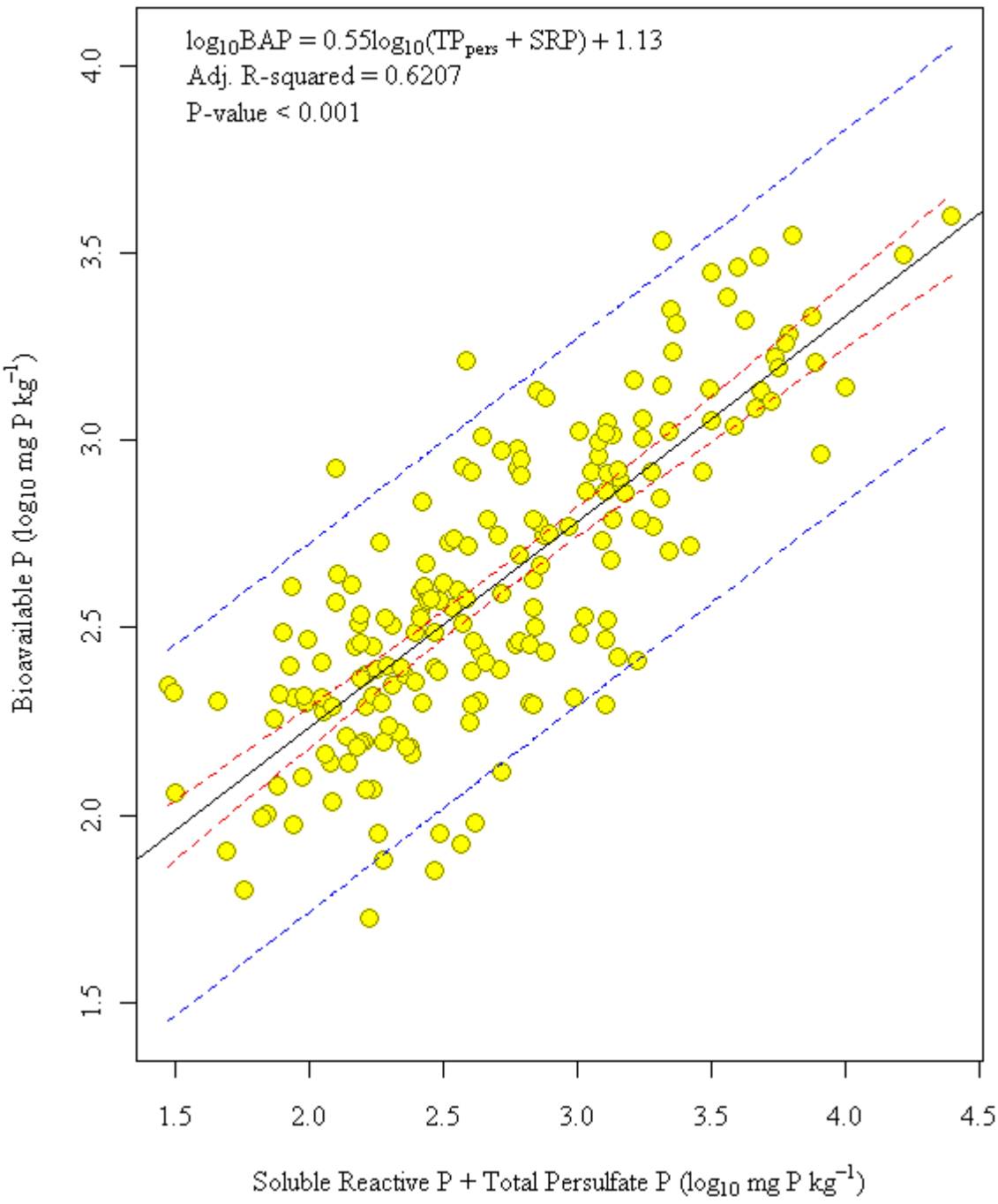

Figure 29. Linear regression model of BAP as a function of TP_{pers} and SRP (Equation 2). Red lines indicate 95% confidence intervals; blue lines indicate 95% prediction intervals.

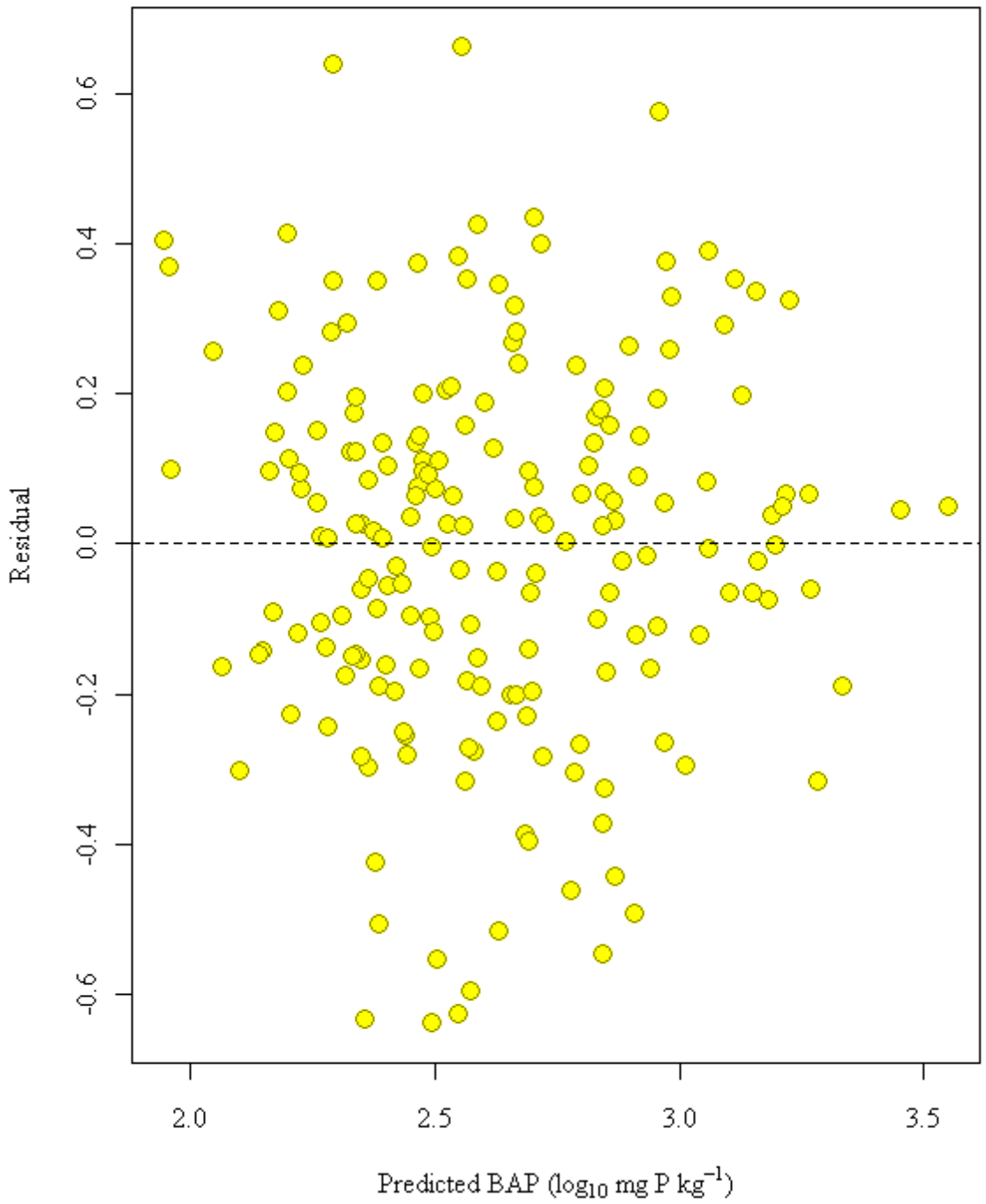

Figure 30. Linear regression model residuals for bivariate linear model predicting BAP as a function of TP_{pers} and SRP (Equation 2).

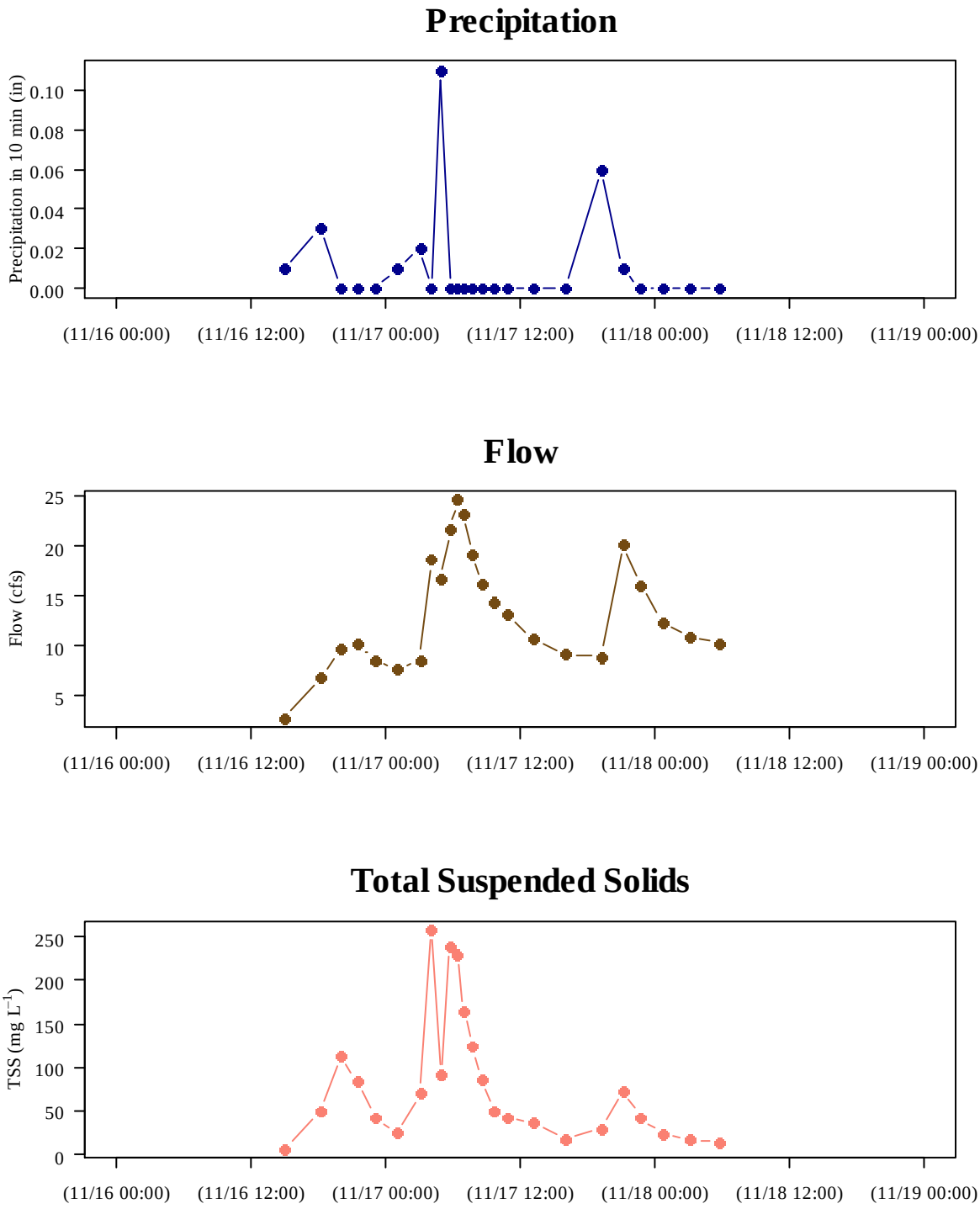

Figure 31. Water quality data for one storm event occurring November 16th, 2009 to November 19th, 2009, used to compare measured stream TP_{pers} to predicted TP_{pers} based on TSS concentrations (stream data provided by R. Matthews, 2010).

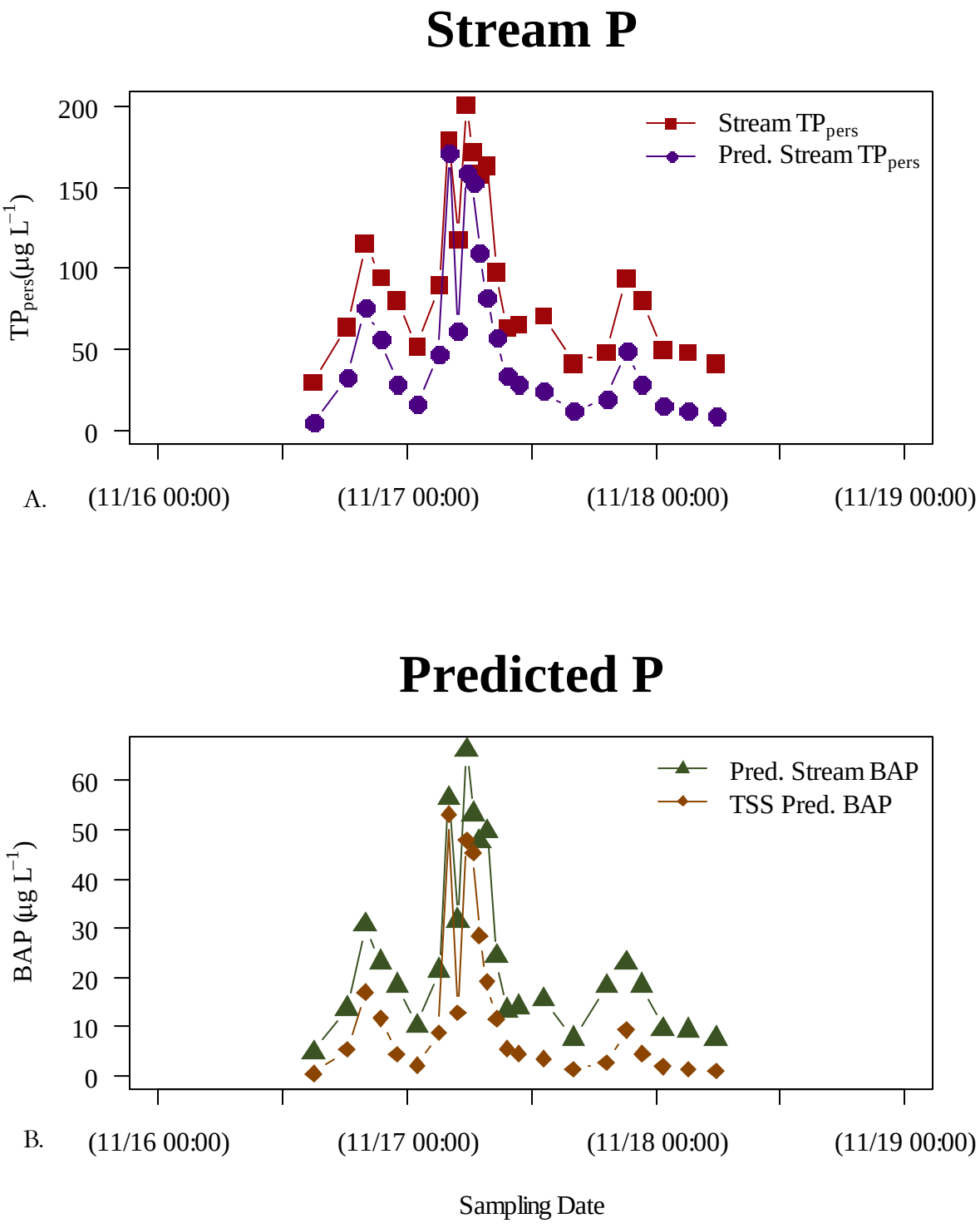

Figure 32. A. Measured stream TP_{pers} compared to predicted stream TP_{pers} based on TSS data. B. BAP predicted from stream TP_{pers} concentrations and BAP predicted using TSS concentrations to predict TP_{pers} concentrations.

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Appendix

Initial Statistical Analysis

Density plots were used to identify transformations that fit sample distributions as closely as possible to the standard normal distribution (Figures A2 – A5). Normality of transformed or untransformed variables was assessed using quantile-quantile plots. If sample quantiles roughly matched theoretical quantiles, sample values were assumed to come from a normal distribution with any mean and standard deviation (Dalgaard, 2002; Figures A6 – A7). Transformations were formally tested by comparing test statistics and p-values of Shapiro-Wilks normality tests to corresponding Shapiro-Wilks test results for untransformed variables. A transformation was retained if the null hypothesis was not rejected or in the case of BAP and TP_{pers}, if the p-value approached the critical value of 0.05.

The $\log_{10}$ transformations were retained for SRP, BAP and TP_{pers} variables. Square root transformations were retained for organic matter, clay and silt variables. The null hypothesis of Shapiro-Wilks normality test was rejected for BAP, TP_{pers}, aspect, elevation, pH, slope and sand while the null hypothesis was not rejected for SRP, organic matter, particle size, clay, and silt (p-value $\leq$ 0.050; Table A4). Because linear regression is known to be relatively robust to minor departures from normality and the large sample size, variables were considered to approach normality due to large sample sizes (n = 195 for SRP, BAP, TP_{pers}, aspect, elevation, organic matter, and pH or n = 65 for particle size, clay, silt and sand).

The null hypothesis of Barlett's test for homogeneity of variances was rejected for SRP, BAP,

TP_{pers}, elevation, and pH variables indicating that variances between soil series within these variables were not the same. The null hypothesis was not rejected for aspect, organic matter, particle size, clay, silt and sand variables indicating that variances between soil series within these variables were not different (Table A5).

A finding of significant difference by analysis of variance indicated that there were differences among soil series within the identified variable. Significant differences between soil series were detected within particle size, SRP, BAP, aspect, elevation, slope and pH (Table A6). Variables found to have significant differences were further analyzed for pairwise differences (Table A7).

The null hypothesis of Bartlett's test for homogeneity of variances was rejected for transformed SRP indicating that variances between size fraction were not the same. The null hypothesis was not rejected for BAP, TP_{pers} and organic matter indicating that variances between size fraction within these variables were not different (Table A8). Particle size, clay, silt and sand were not included in this test because they were only measured within the "small" size fraction due to constraints of the analytical method. A finding of significant difference by analysis of variance indicated that there were differences among size fraction within the identified variable. Significant differences were detected within organic matter and TP_{pers} (Table A9).

Correlation analysis showed that phosphorus measures were positively correlated. Principal components analysis had similar results, indicating that one P measure (e.g. TP_{pers}) can be used to predict the others (e.g. SRP and BAP).

Correlation Analysis

Correlation analysis is used to identify covariation between variables, meaning that one variable changes, in either a positive or negative direction, as another variable changes, in either a positive or negative direction, without implying a dependent or causal relationship between the two variables. Kendall's τ is used to calculate a correlation coefficient according to the formula:

$$\tau = \frac{S}{\left[\frac{n(n-1)}{2}\right]}$$

where $S = P - M$, P = number of times y increases with x, M = number of times y decreases as x increases. When there is perfect correlation, τ will be -1 for a negative correlation or 1 for a positive correlation between variables. When there is no correlation between variables, τ will be 0. This statistic avoids the use of the normal distribution, which many of the variables in this data set do not follow, and is instead based on a ratio between the number of times y increases as x increases or decreases and sample size. Significance testing is performed on the null hypothesis that $\tau = 0$, indicating there is no significant change in slope between x and y variables, and the alternative hypothesis that $\tau \neq 0$, indicating either a positive or negative significant change in slope between x and y variables. This statistic is vulnerable to the same phenomenon as other correlation coefficients in that significant correlations can simply be found by increasing sample size. Because τ is ranked based, it will not change according to power transformations of either x or y variables. Strong correlations correspond to τ values around or above 0.7. Kendall's τ is preferred over other correlation coefficients like Spearman's ϱ due to relative ease of interpretation and large sample approximation procedure for $n > 10$. In addition, τ is resistant to outliers and measures linear and non-linear relationships (Dalgaard, 2002; Everitt and Hothorn, 2006; Helsel and Hirsch, 2002).

Principal Components Analysis

Principal component analysis is a statistical technique that attempts to explain the variation seen between a set of correlated variables by grouping them in such a way that the most amount of variation is accounted for in the first component. Subsequent combinations of variables are constructed according to the number of variables included in the analysis, but each component should account for less and less variation. The goal of this type of analysis is for the first few components to account for a substantial amount of variation seen in the original variables and provide a useful summary of those variables that most influence a variable of interest. Construction of each component is accomplished through the calculation of an eigenvector based on the correlation matrix, so that results are not simply influenced by differences in magnitude of unit of measure between variable. However, this places equal importance on each variable, which may or may not be appropriate.

Components can be labeled according to user interpretation of their coefficients, but this is not a formal procedure as employed in this study. Semi-formal methods do exist, and can require a nuanced understanding of the relationships between variables, which seemingly defeats the value of PCA for exploratory multivariate data analysis. If interpretation of component coefficients lends itself to the creation of labels, then this process can be helpful in understanding the role groups of variables may play in influencing and possibly explaining each other. Readers should consult Everitt (2005) for a more elaborate discussion.

The examination of these relationships provides information about the links between different forms of phosphorus, potential differences between soil series and potential differences between the amounts of phosphorus in different size fractions. Quantification of the different forms of phosphorus provided baseline data about the amount of phosphorus in approximately half of the Lake Whatcom watershed. Additionally, different forms of phosphorus will become more or less available under shifting environmental conditions, so an understanding of those dynamics will help managers understand the amount and type of phosphorus being delivered to Lake Whatcom and make appropriately informed decisions.

Tables

Table A1. Summary statistics for all variables by soil series.

Soil Property		Chuckanut	Sehome	Squalicum	Squires	Wickersham
tp_{pers}	min	171	240	251	369	343
	median	664	619	692	959	632
	mean	893	678	1015	1059	703
	max	3648	1628	3648	2883	1944
	n	45	36	39	45	30
bap	min	80	63	53	130	83
	median	411	319	521	558	207
	mean	784	392	840	758	315
	max	3407	1150	3994	3547	1816
	n	45	36	39	45	30
srp	min	0.11	0.05	0.16	0.28	0.16
	median	0.50	0.42	0.82	1.03	0.64
	mean	0.84	0.49	1.75	1.11	0.87
	max	3.29	1.83	8.36	5.26	3.30
	n	45	36	39	45	30
aspect	min	0.38	0.21	0.70	0.21	0.35
	median	2.72	2.61	3.35	3.14	4.59
	mean	2.61	3.10	3.38	3.24	4.06
	max	4.99	6.20	5.76	6.00	6.11
	n	45	36	39	45	30
om	min	0.77	0.67	0.93	0.24	0.57
	median	3.00	2.50	2.54	3.44	3.42
	mean	3.00	3.12	2.84	3.53	3.99
	max	12.0	7.49	5.87	7.33	10.64
	n	45	36	39	45	30

Table A1 continued. Summary statistics for all variables by soil series.

Soil Property		Chuckanut	Sehome	Squalicum	Squires	Wickersham
elevation	min	91	102	110	150	95
	median	171	136	212	237	104
	mean	168	158	202	287	105
	max	244	259	381	511	111
	n	45	36	39	45	30
ph	min	4.50	4.19	5.50	4.30	4.10
	median	5.40	4.93	6.20	5.00	5.40
	mean	5.70	5.11	6.10	4.90	5.30
	max	7.30	6.12	6.60	5.70	6.20
	n	45	36	39	45	30
slope	min	0	2	1	12	0
	median	23	13	20	42	5
	mean	28	25	26	40	10
	max	68	85	75	85	55
	n	45	36	39	45	30
psd	min	252	153	238	267	256
	median	308	293	292	332	335
	mean	305	280	291	333	330
	max	358	342	335	391	378
	n	15	12	13	15	10
sand	min	62	50	70	62	63
	median	81	82	78	82	82
	mean	78	78	80	80	78
	max	89	91	92	94	86
	n	15	12	13	15	10

Table A1 continued. Summary statistics for all variables by soil series.

Soil Property		Chuckanut	Sehome	Squalicum	Squires	Wickersham
silt	min	10	8	8	6	13
	median	19	17	21	18	18
	mean	21	21	19	19	20
	max	36	46	27	36	35
	n	15	12	13	15	10
clay	min	0.23	0.00	0.00	0.02	0.16
	median	0.94	0.66	1.17	0.48	0.68
	mean	1.15	1.07	1.14	0.73	0.71
	max	2.40	3.37	2.36	1.94	1.74
	n	15	12	13	15	10

Table A2. Summary statistics for all variables by size fraction.

Soil Property		Small	Medium	Large
tp_{pers}	min	171	210	266
	median	649	718	662
	mean	723	964	992
	max	2036	3312	3648
	n	65	65	65
bap	min	53	71	76
	median	356	411	294
	mean	564	709	660
	max	2060	3115	3994
	n	65	65	65
srp	min	0.12	0.21	0.05
	median	0.63	0.55	0.64
	mean	1.28	0.77	1.01
	max	8.36	3.29	6.81
	n	65	65	65
aspect	min	0.21	0.21	0.21
	median	3.04	3.04	3.04
	mean	3.23	3.23	3.23
	max	6.20	6.20	6.20
	n	65	65	65
om	min	0.67	1.22	0.24
	median	3.25	3.67	2.08
	mean	3.86	3.85	2.24
	max	10.64	12.07	9.50
	n	65	65	65

*not analyzed

Table A2 continued. Summary statistics for all variables by size fraction.

Soil Property		Small	Medium	Large
elevation	min	91	91	91
	median	165	165	165
	mean	191	191	191
	max	511	511	511
	n	65	65	65
ph	min	4.10	4.10	4.10
	median	5.40	5.40	5.40
	mean	5.40	5.40	5.40
	max	7.30	7.30	7.30
	n	65	65	65
slope	min	0	0	0
	median	20	20	20
	mean	27	27	27
	max	85	85	85
	n	65	65	65
psd	min	153	*	*
	median	308	*	*
	mean	308	*	*
	max	391	*	*
	n	65	*	*
sand	min	50	*	*
	median	81	*	*
	mean	79	*	*
	max	94	*	*
	n	65	*	*

*not analyzed

Table A2 continued. Summary statistics for all variables by size fraction.

Soil Property		Small	Medium	Large
silt	min	6	*	*
	median	18	*	*
	mean	20	*	*
	max	46	*	*
	n	65	*	*
clay	min	0	*	*
	median	0.79	*	*
	mean	0.97	*	*
	max	3.37	*	*
	n	65	*	*

*not analyzed

Table A3. Significant results of Shapiro-Wilks Normality Test, (p-value ≤ 0.05). Non-significant p-values were omitted.

Transformed Analyte	P-value	Conclusion
$\log_{10}$srp		Fail to reject H_0
$\log_{10}$bap	0.018	Reject H_0
$\log_{10}tp_{pers}$	0.049	Reject H_0
aspect	<0.001	Reject H_0
elevation	<0.001	Reject H_0
ph	0.001	Reject H_0
$\sqrt{\text{om}}$		Fail to reject H_0
slope	<0.001	Reject H_0
psd		Fail to reject H_0
$\sqrt{\text{clay}}$		Fail to reject H_0
$\sqrt{\text{silt}}$		Fail to reject H_0
sand	0.010	Reject H_0

Table A4. Significant results of Bartlett's test for homogeneity of variance test results, (p-value ≤ 0.05). Non-significant p-values were omitted.

H_0: variances in each Soil series are the same
H_a: variances in one or more Soil series are not the same

Transformed Analyte	P-value	Conclusion
$\log_{10}$srp	0.015	Reject H_0
$\log_{10}$bap	0.014	Reject H_0
$\log_{10}tp_{pers}$	<0.001	Reject H_0
aspect		Fail to reject H_0
elevation	<0.001	Reject H_0
ph	<0.001	Reject H_0
$\sqrt{\text{om}}$		Fail to reject H_0
slope	0.009	Reject H_0
psd		Fail to reject H_0
$\sqrt{\text{clay}}$		Fail to reject H_0
$\sqrt{\text{silt}}$		Fail to reject H_0
sand		Fail to reject H_0

Table A5. Analysis of variance table showing significant differences within soil series (p-value ≤ 0.05). Variables were assumed to have equal variances if the null hypothesis of Bartlett's test was not rejected. The opposite was true if the null hypothesis of Bartlett's test was rejected. Non-significant p-values were omitted.

Response Factor	P-value	Conclusion
$\sqrt{\text{om}}$		Fail to reject H_0
$\sqrt{\text{clay}}$		Fail to reject H_0
$\sqrt{\text{silt}}$		Fail to reject H_0
sand		Fail to reject H_0
psd	0.003	Reject H_0
$\log_{10}$ srp	<0.001	Reject H_0
$\log_{10}$ naoh p	<0.001	Reject H_0
$\log_{10} \text{tp}_{\text{pers}}$	<0.001	Reject H_0
aspect	0.015	Reject H_0
elevation	<0.001	Reject H_0
slope	<0.001	Reject H_0
ph	<0.001	Reject H_0

Table A6. Pairwise t-tests between variables with significant differences (p-value ≤ 0.05) among soil series using Holm's correction. This test identified the location of significant differences between soil series among variables identified by ANOVA testing. Pooled variances were used when the variable did not reject the null hypothesis of Bartlett's test for Homogeneity of Variance. Non-significant p-values were omitted.

Response Factor		Soil Series			
		Chuckanut	Sehome	Squalicum	Squires
psd	Sehome		–	–	–
	Squalicum			–	–
	Squires		0.010		–
	Wickersham		0.039		
$\log_{10}$ srp	Sehome		–	–	–
	Squalicum		<0.001	–	–
	Squires		<0.001		–
	Wickersham				
$\log_{10}$ bap	Sehome	0.033	–	–	–
	Squalicum			–	–
	Squires		0.003		–
	Wickersham	0.001		0.015	<0.001
$\log_{10}$ tp_{pers}	Sehome		–	–	–
	Squalicum			–	–
	Squires		<0.001		–
	Wickersham				0.001
aspect	Sehome		–	–	–
	Squalicum			–	–
	Squires				–
	Wickersham	0.014			
elevation	Sehome		–	–	–
	Squalicum		0.034	–	–
	Squires	<0.001	<0.001	0.002	–
	Wickersham	<0.001	<0.001	<0.001	<0.001
slope	Sehome		–	–	–
	Squalicum			–	–
	Squires	0.041	0.041	0.024	–
	Wickersham	<0.001	0.041	0.014	<0.001
ph	Sehome	0.006	–	–	–
	Squalicum	0.017	<0.001	–	–
	Squires	<0.001		<0.001	–
	Wickersham			<0.001	

Table A7. Homogeneity of variance test results of the only variables that actually varied within size fraction, (p-value < 0.05). Non-significant p-values were omitted.

H_0: variances of the variable and Size Fraction are the same H_a: variances of the variable and Size Fraction are not the same		
Response Factor	P-value	Conclusion
$\log_{10}$ srp	0.002	Reject H_0
$\log_{10}$ bap		Fail to reject H_0
$\log_{10} tp_{pers}$		Fail to reject H_0
$\sqrt{om}$		Fail to reject H_0

Table A8. Analysis of variance table showing differences within size fractions (p-value ≤ 0.05).Variables were assumed to have equal variances if the null hypothesis of Bartlett's test was not rejected. The opposite was true if the null hypothesis of Bartlett's test was rejected. Non-significant p-values were omitted.

Response Factor	DF	F value	P-value
$\log_{10}$ srp	2	1.122	
$\sqrt{\text{om}}$	2	18.732	<0.001
$\log_{10}$ bap	2	1.236	
$\log_{10} \text{tp}_{\text{pers}}$	2	4.580	0.012

Table A9. Pairwise t-tests between variables with significant differences among size fractions using Holm's correction (p-value $\leq$ 0.05). This test identified the location of significant differences between soil series among variables identified by ANOVA testing. Pooled variances were used when the variable did not reject the null hypothesis of Bartlett's test for Homogeneity of Variance. Non-significant p-values were omitted.

Response Factor		Size Fraction	
		Large	Medium
$\sqrt{\text{om}}$	Medium	<0.001	–
	Small	<0.001	
$\log_{10} \text{tp}_{\text{pers}}$	Medium		–
	Small	0.030	0.030

Figures

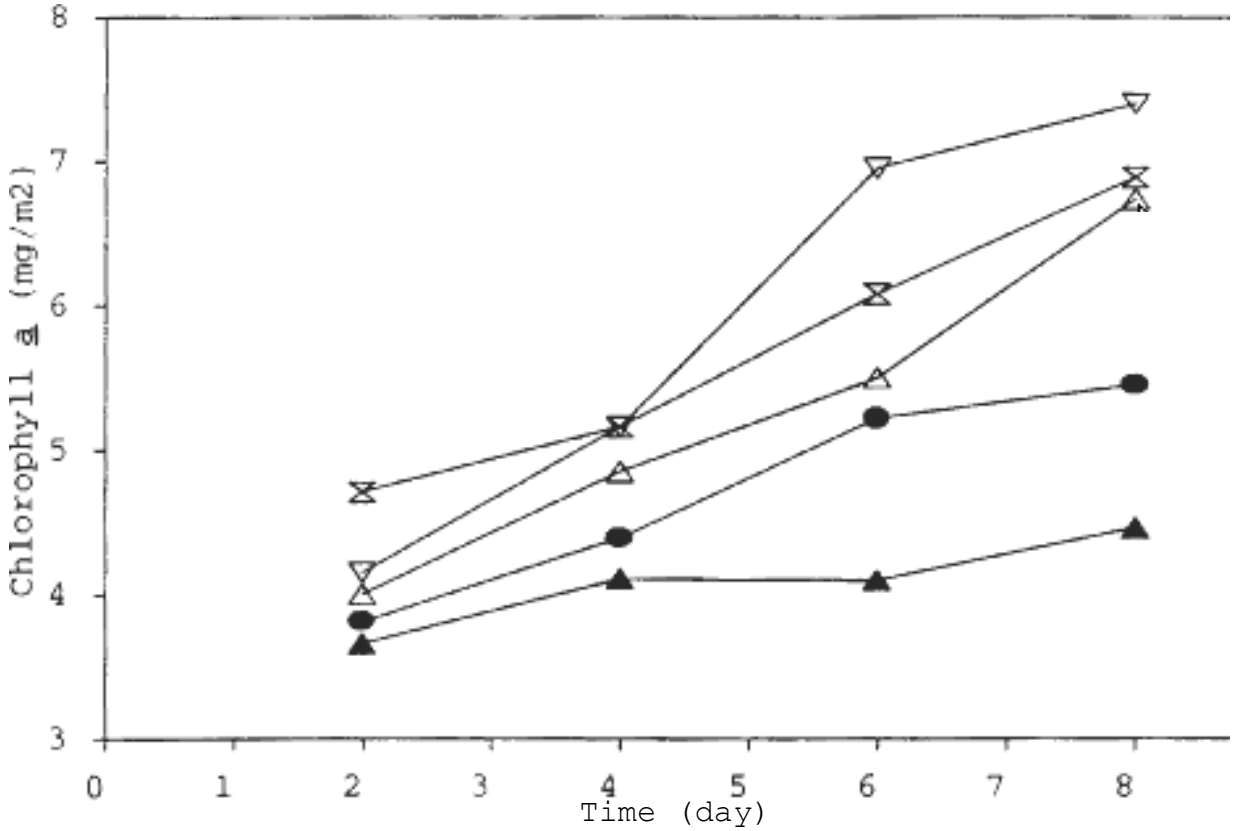

Figure A1. Chlorophyll *a* concentration over time in samples enriched with soil: ▲control, ● 62 mg soil, Δ 186 mg soil, ⋈ 310 mg soil, ∇ 620 mg soil. November 1992 (Liang, 1994).

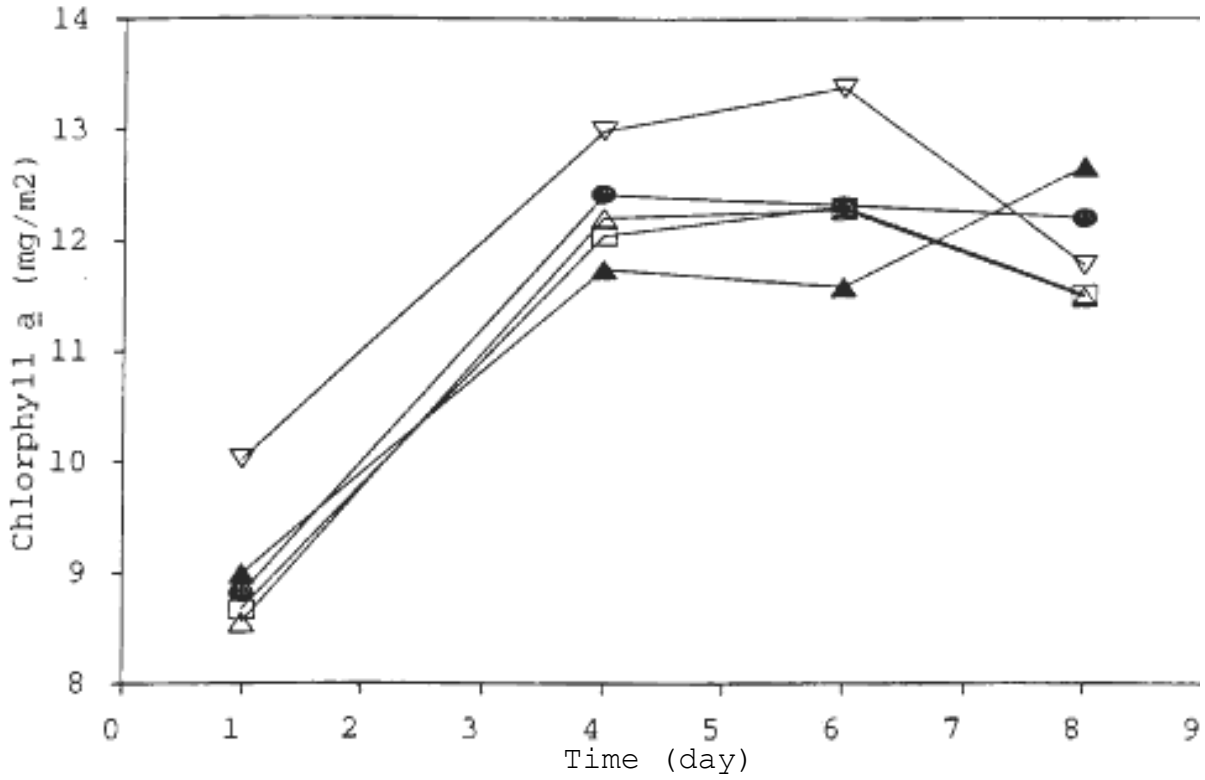

Figure A2. Chlorophyll *a* concentration over time in samples enriched with different concentrations of phosphorus and with soil: ▲control, ● 10 µg L^{-1} $P0_4$-P, Δ 30 µg L^{-1} $P0_4$-P, □ 50 µg L^{-1} $P0_4$-P, ∇ 620 mg soil. February 1993 (Liang, 1994).

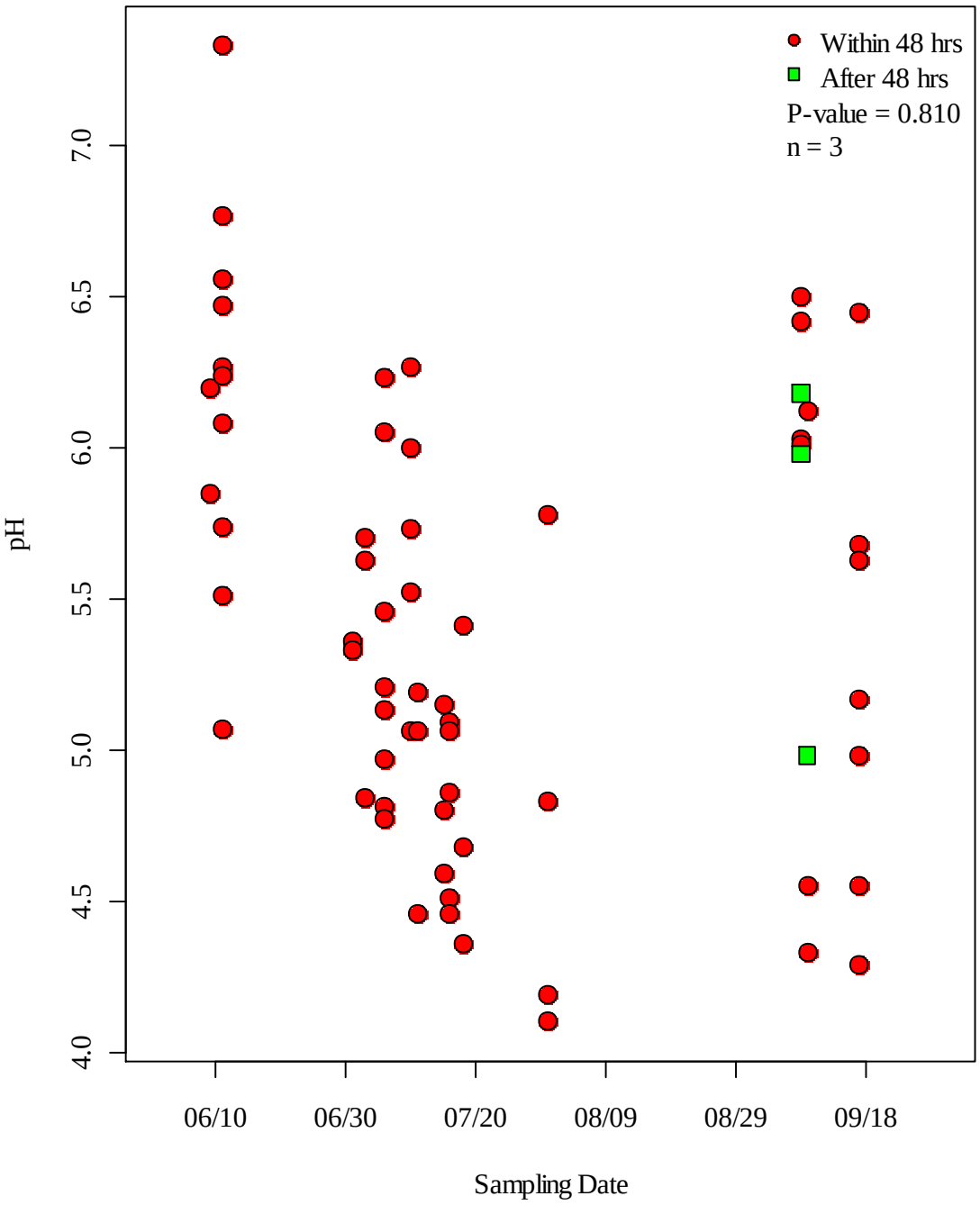

Figure A3. Comparison between pH samples analyzed within 48 hrs and samples that were frozen, thawed, and analyzed.

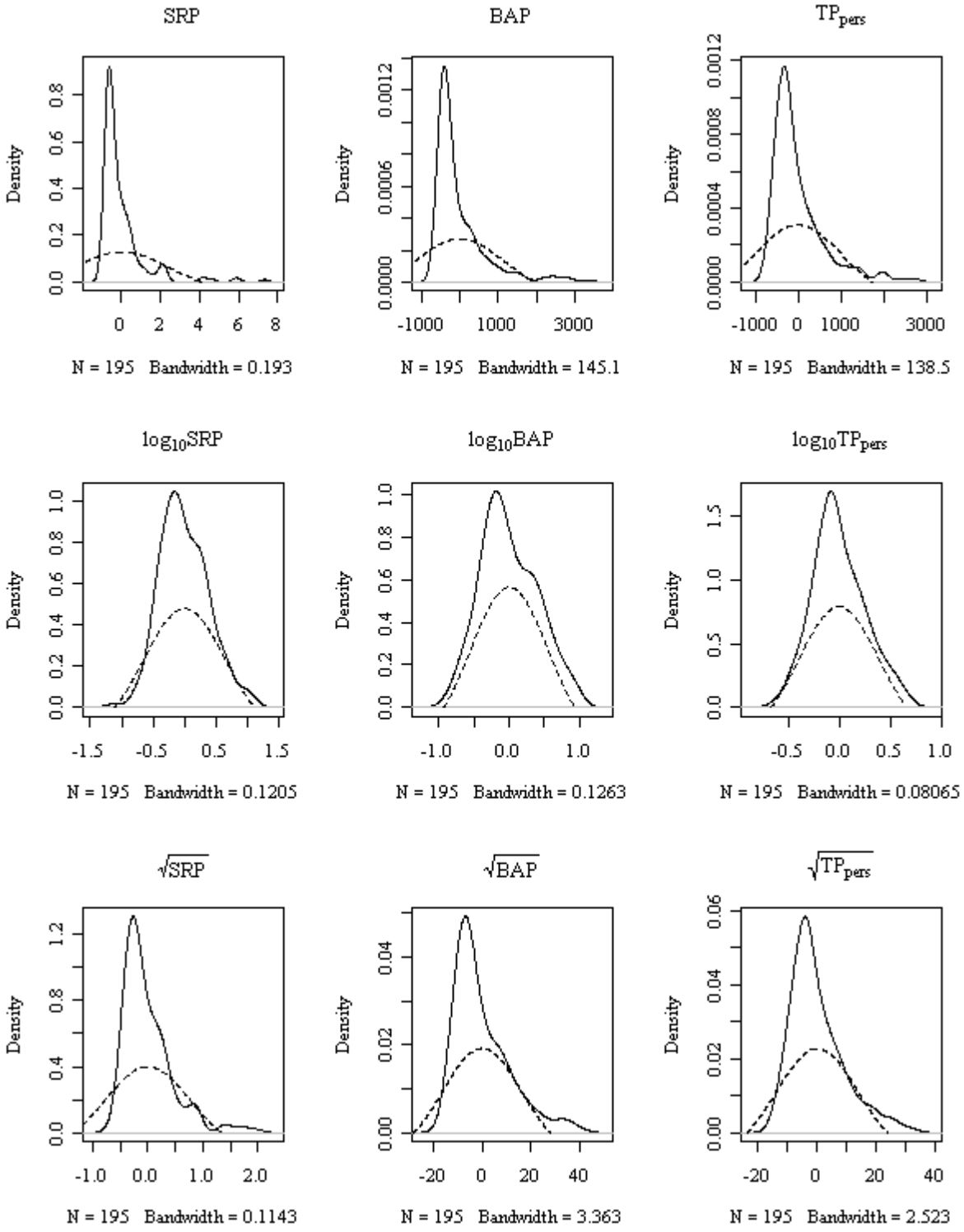

Figure A4. Density plots for untransformed, $\log_{10}$ and square root transformations of sample variables compared to standard normal distributions with the same mean and standard deviation as the sample distributions.

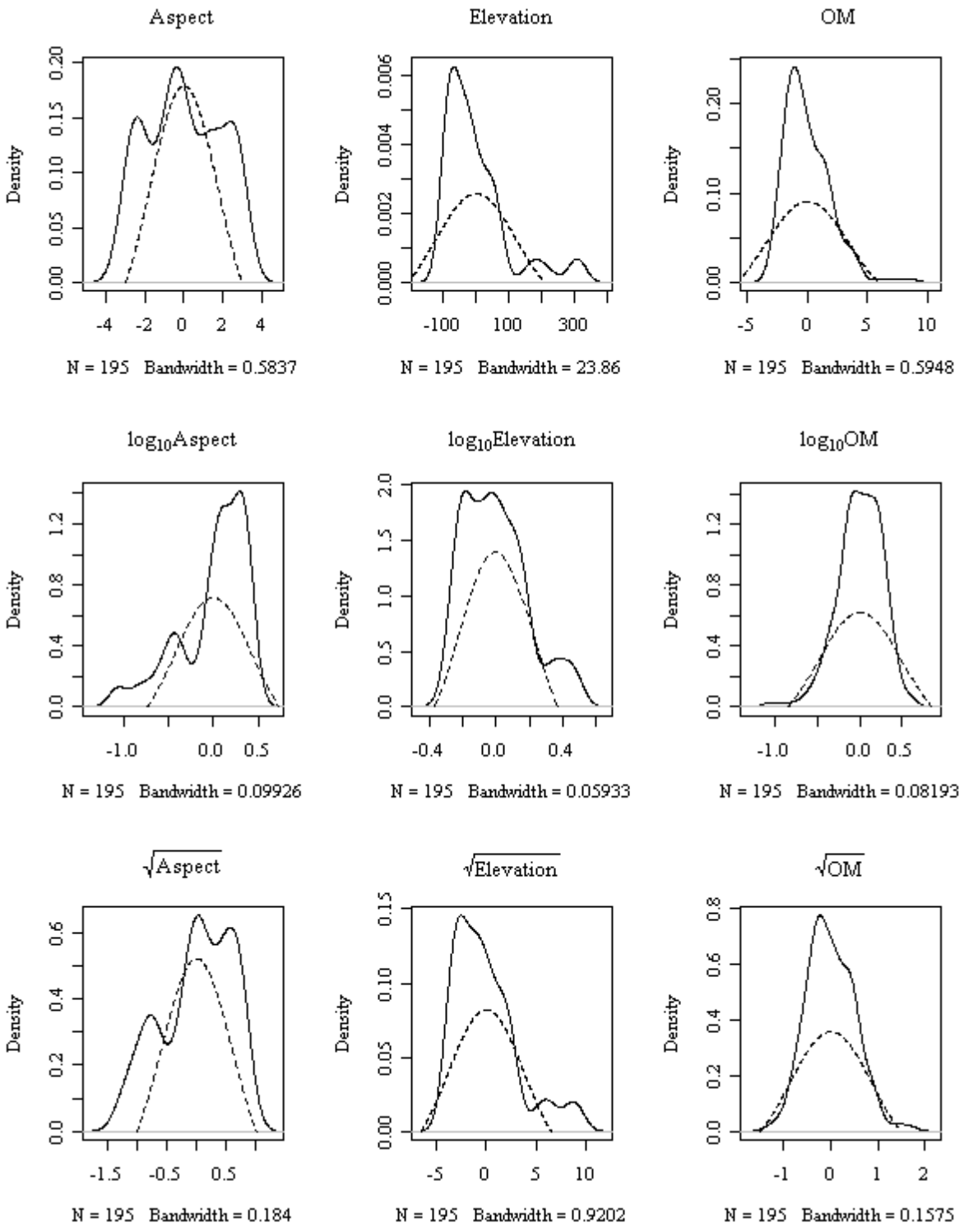

Figure A4 continued. Density plots for untransformed, $\log_{10}$ and square root transformations compared to standard normal distributions with the same mean and standard deviation as the sample distributions.

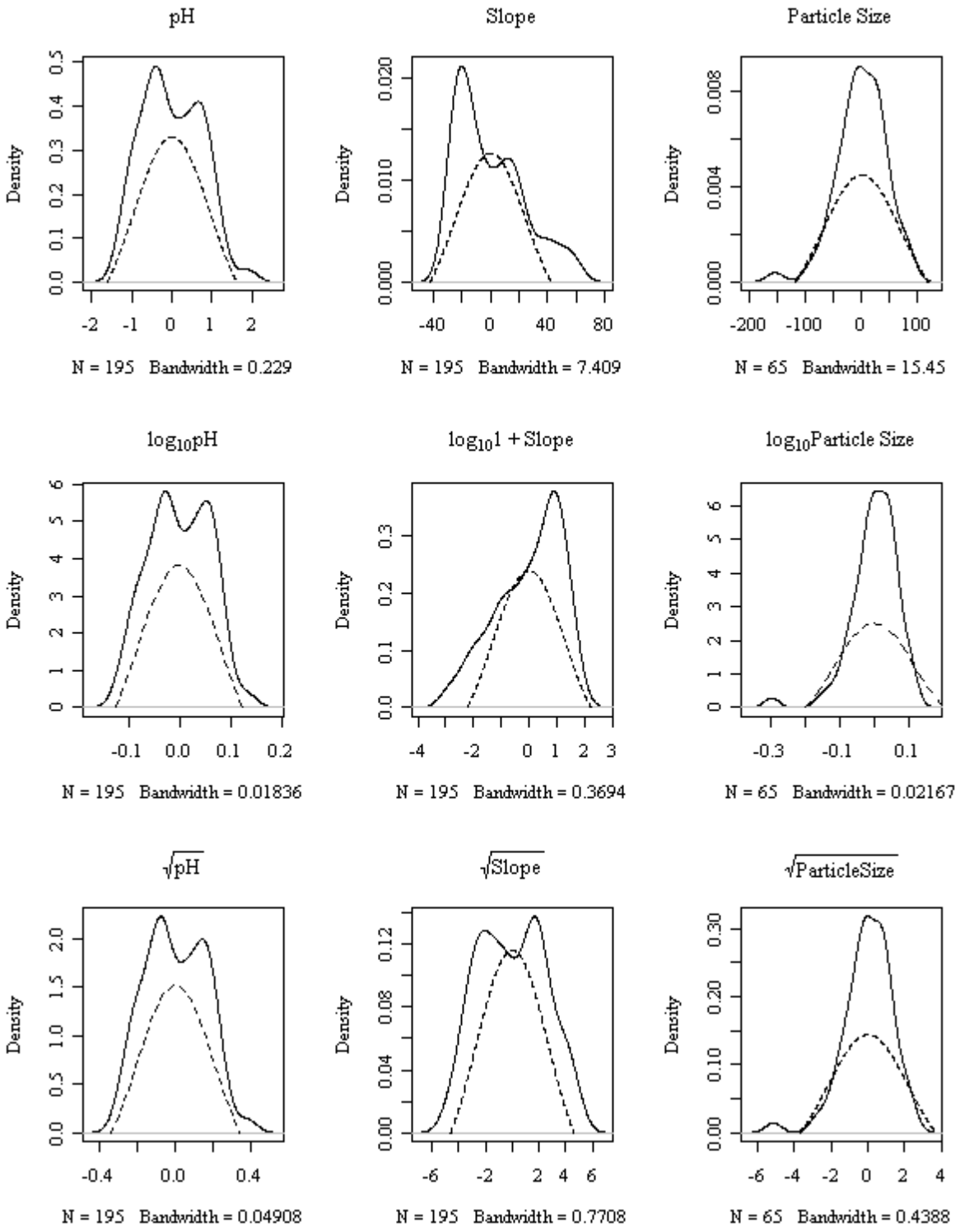

Figure A4 continued. Density plots for untransformed, $\log_{10}$ and square root transformations compared to standard normal distributions with the same mean and standard deviation as the sample distributions.

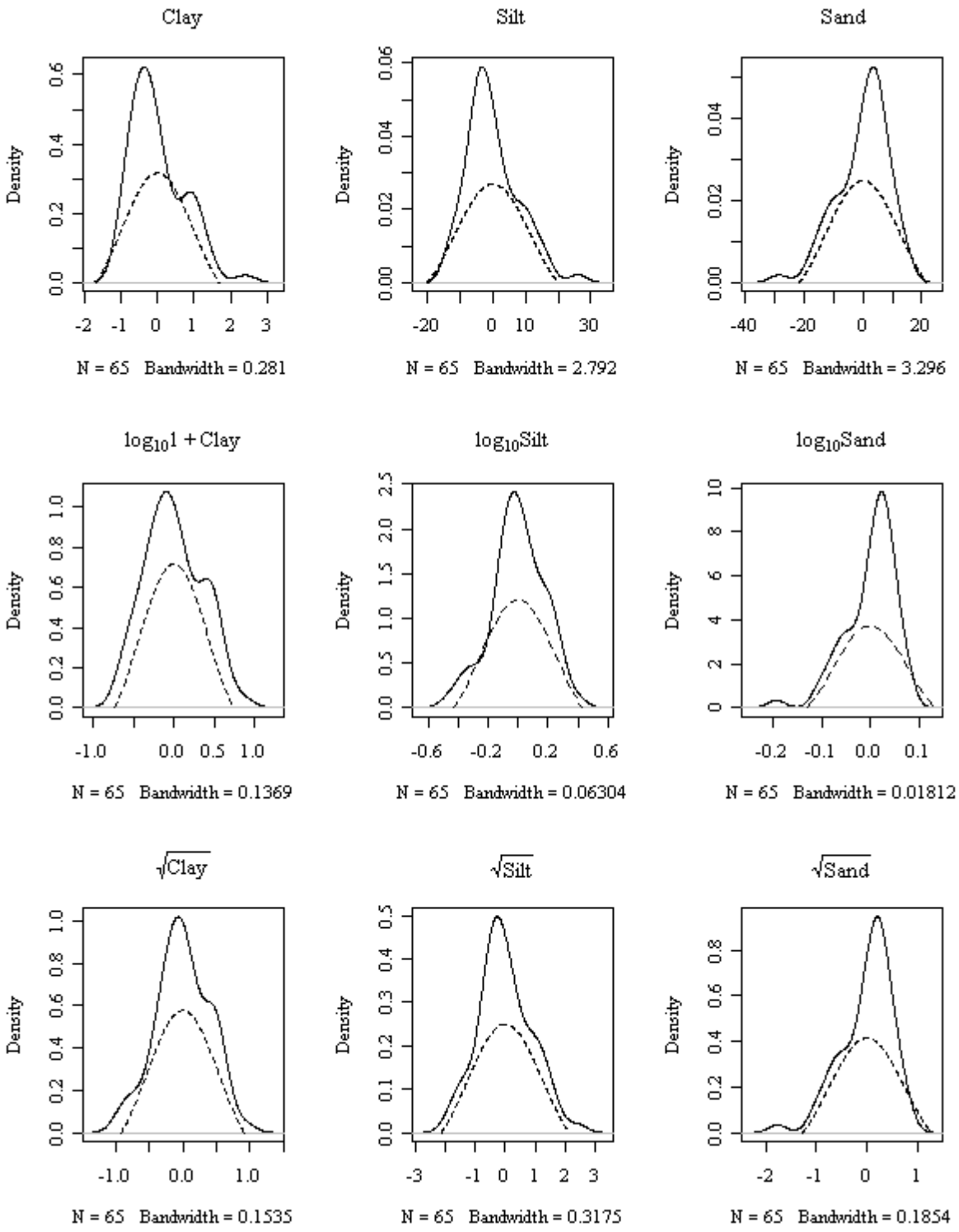

Figure A4 continued. Density plots for untransformed, $\log_{10}$ and square root transformations compared to standard normal distributions with the same mean and standard deviation as the sample distributions.

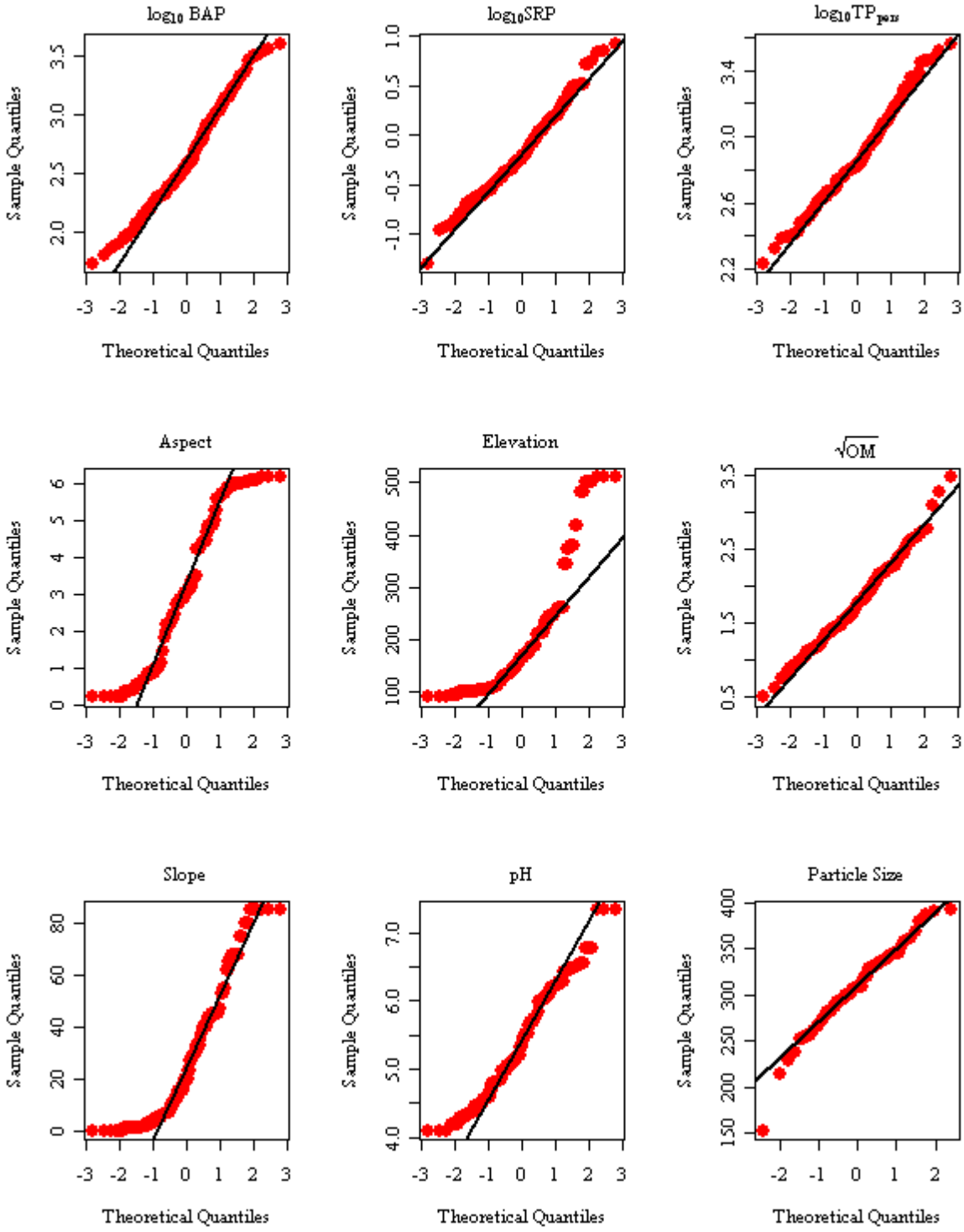

Figure A5. Normal probability plots for transformed or untransformed variables. If the sample quantiles roughly matched theoretical quantiles by following a straight line when plotted against each other, then the sample approximates a normal distribution.

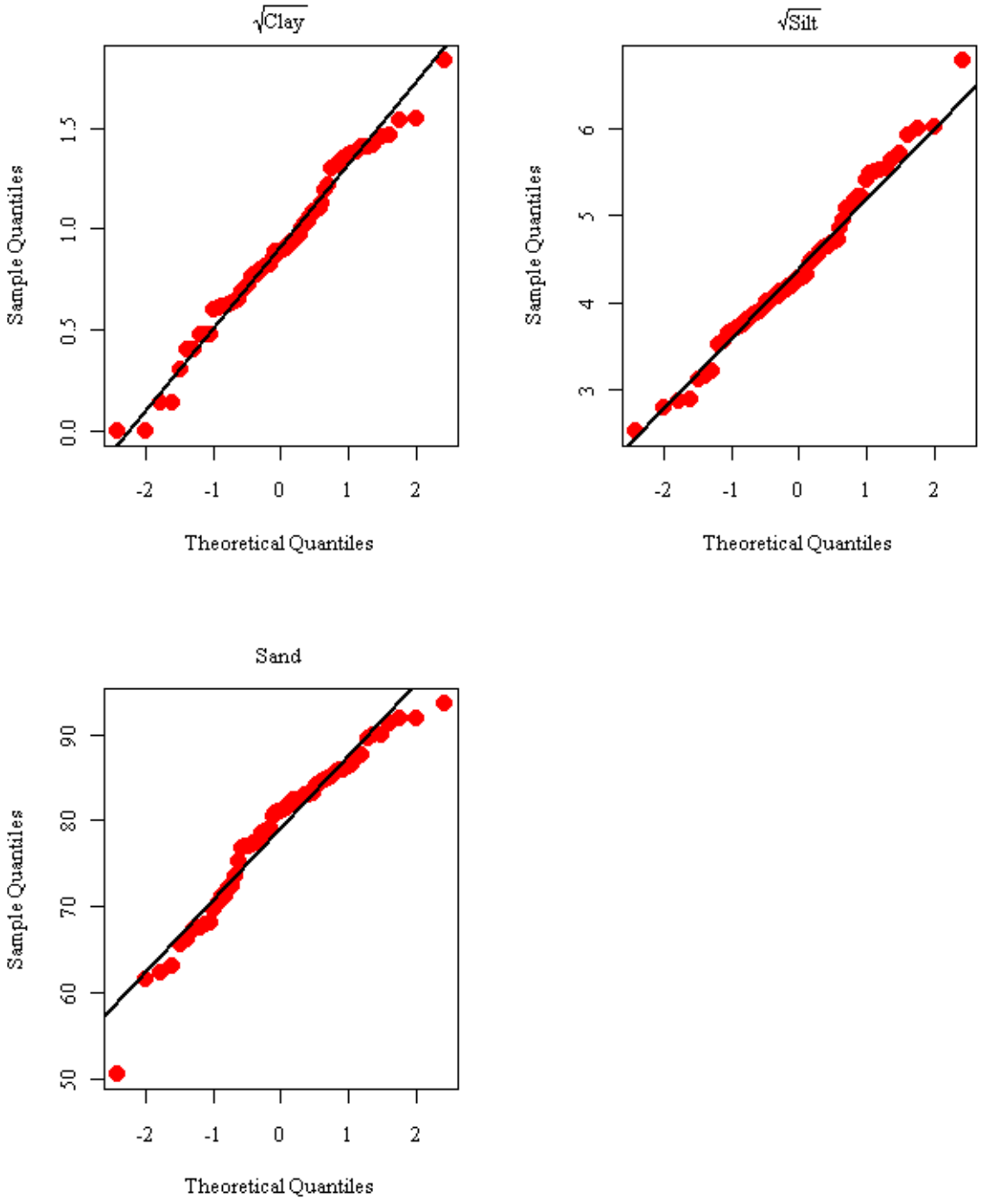

Figure A5 continued. Normal probability plots for all normally distributed transformed or untransformed variables. If the sample quantiles roughly matched theoretical quantiles by following a straight line when plotted against each other, then the sample approximates a normal distribution.

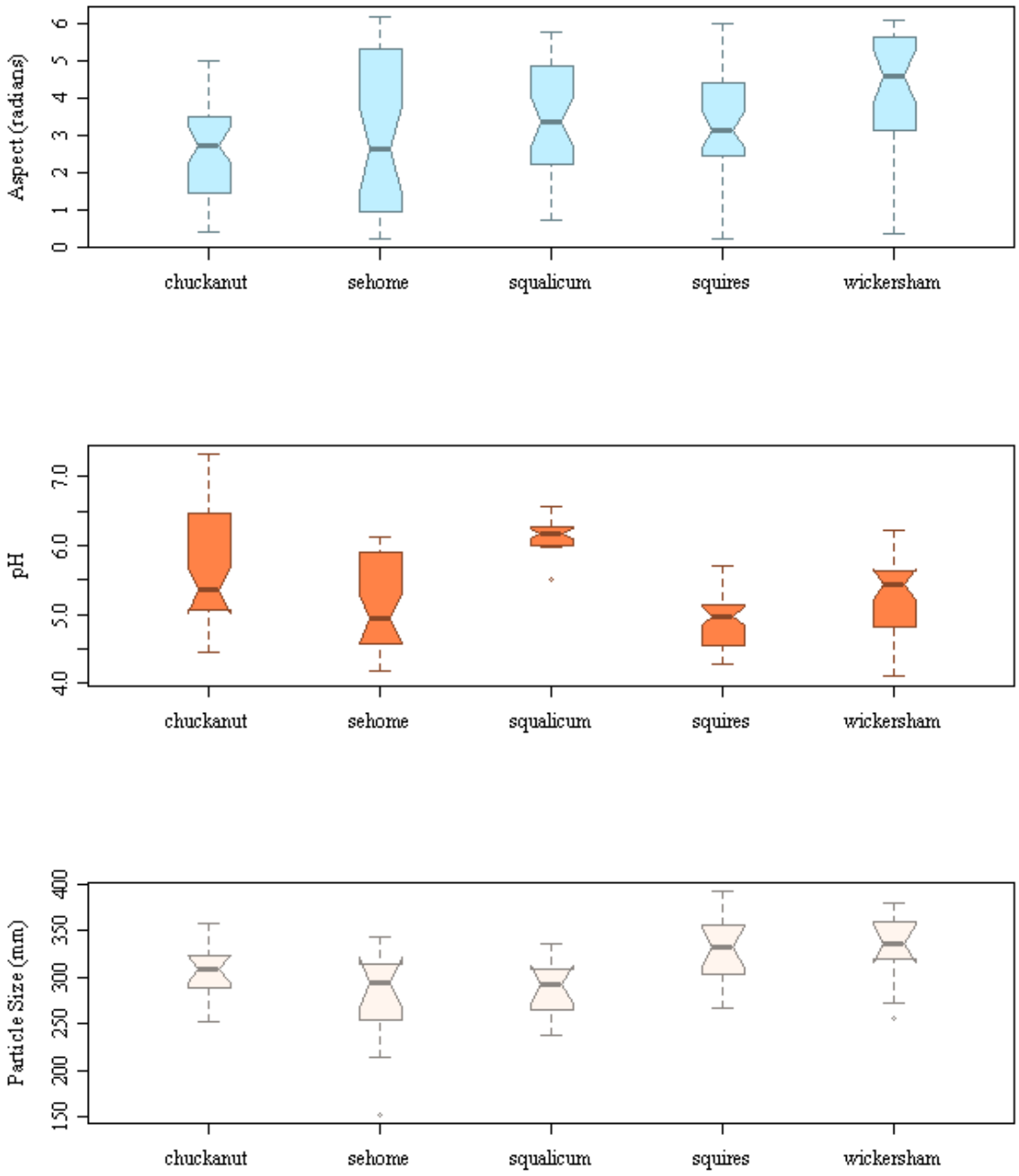

Figure A6. Boxplots showing relationships between aspect, pH, particle size and soil series in soil samples from the Lake Whatcom watershed. Overlapping notches show pairs that are not significantly different (Dalgaard, 2002).

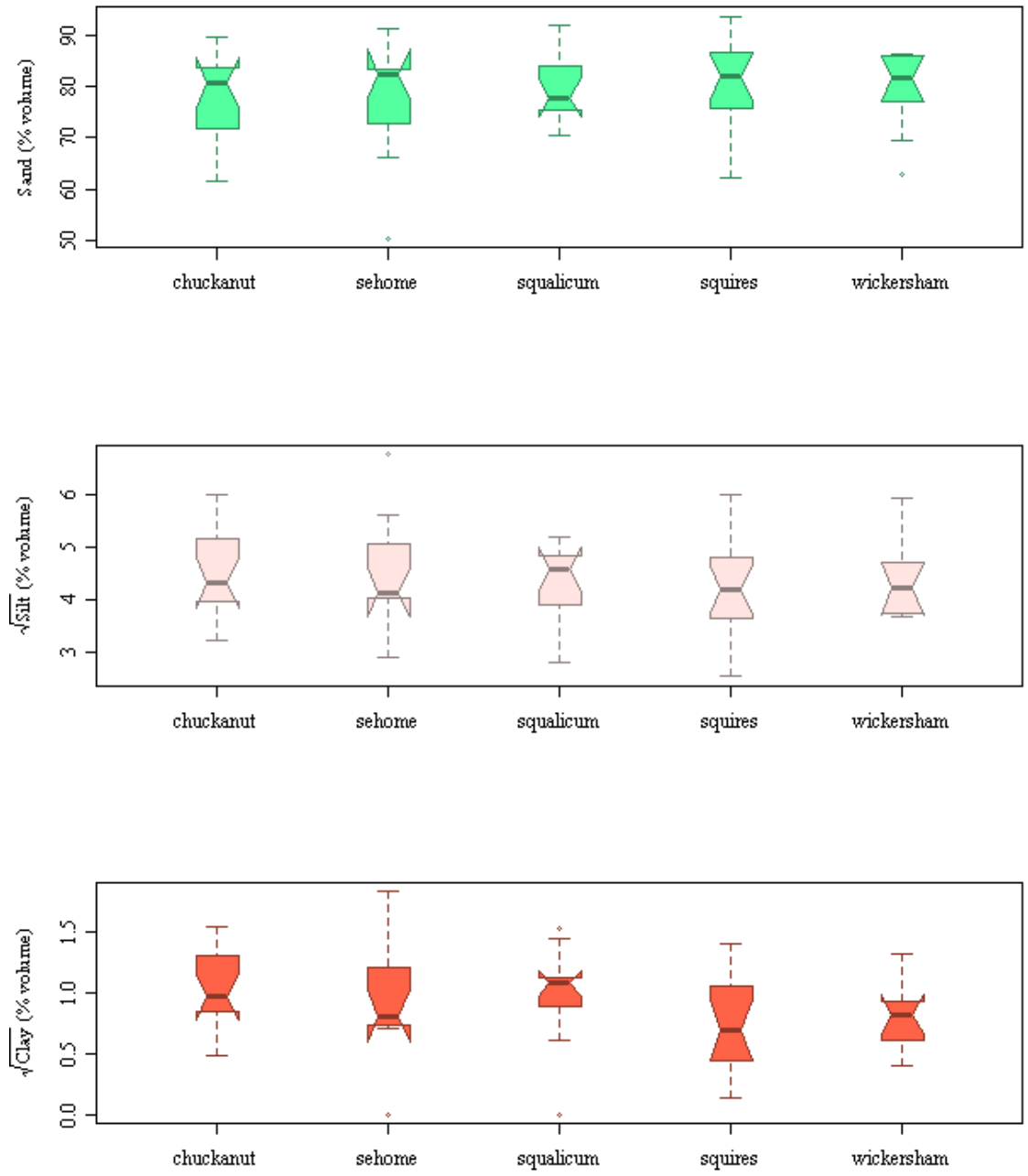

Figure A7. Boxplots showing relationships between sand, silt, clay and soil series in soil samples from the Lake Whatcom watershed. Overlapping notches show pairs that are not significantly different (Dalgaard, 2002).

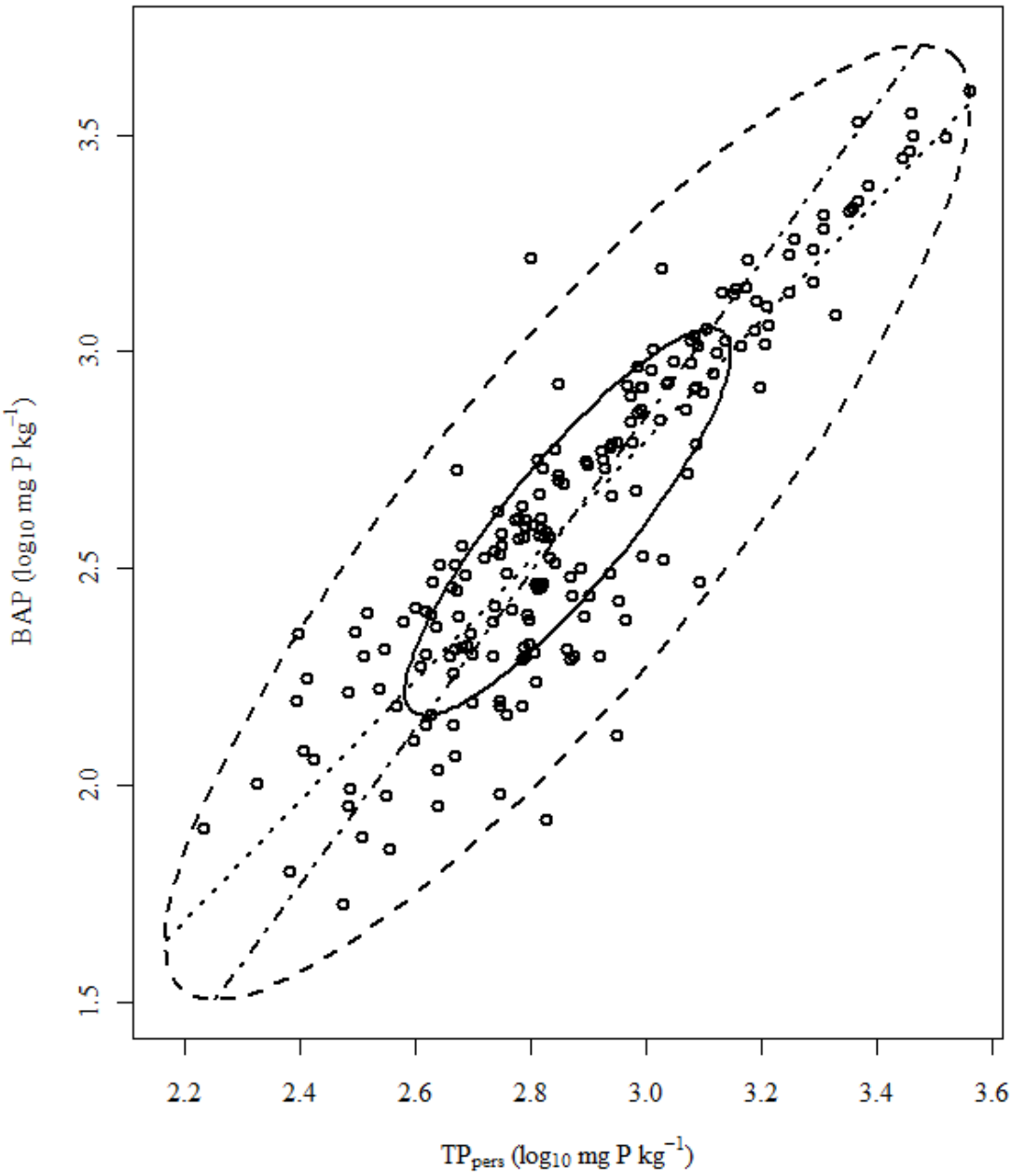

Figure A8. Bivariate boxplot comparing $\log_{10}$ transformed bap and tp_{pers} variables. This plot was a two dimensional analogue of the boxplot typically used for univariate data. The inner circle indicates the location of 50% of the data while the outer circle delineates potential outliers. Regression lines were also drawn for both variables. The intersection of regression lines showed the bivariate location estimator while the angle of intersection indicated the degree of correlation between the variables. A small angle indicated high correlation while a large angle indicated small correlation (Everitt, 2005).

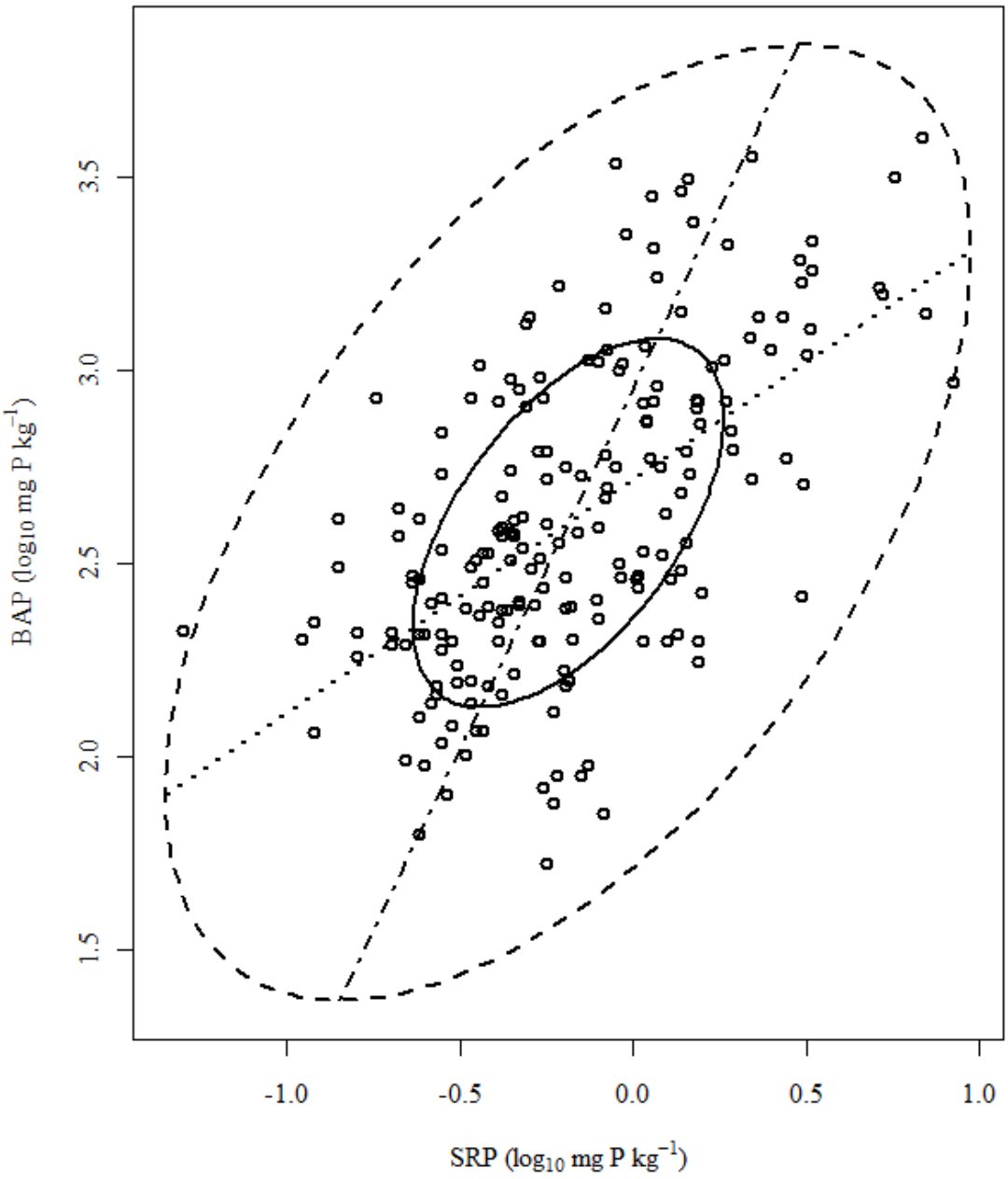

Figure A9. Bivariate boxplot comparing $\log_{10}$ transformed bap and srp variables. This plot was a two dimensional analogue of the boxplot typically used for univariate data. The inner circle indicates the location of 50% of the data while the outer circle delineates potential outliers. Regression lines were also drawn for both variables. The intersection of regression lines showed the bivariate location estimator while the angle of intersection indicated the degree of correlation between the variables. A small angle indicated high correlation while a large angle indicated small correlation (Everitt, 2005).

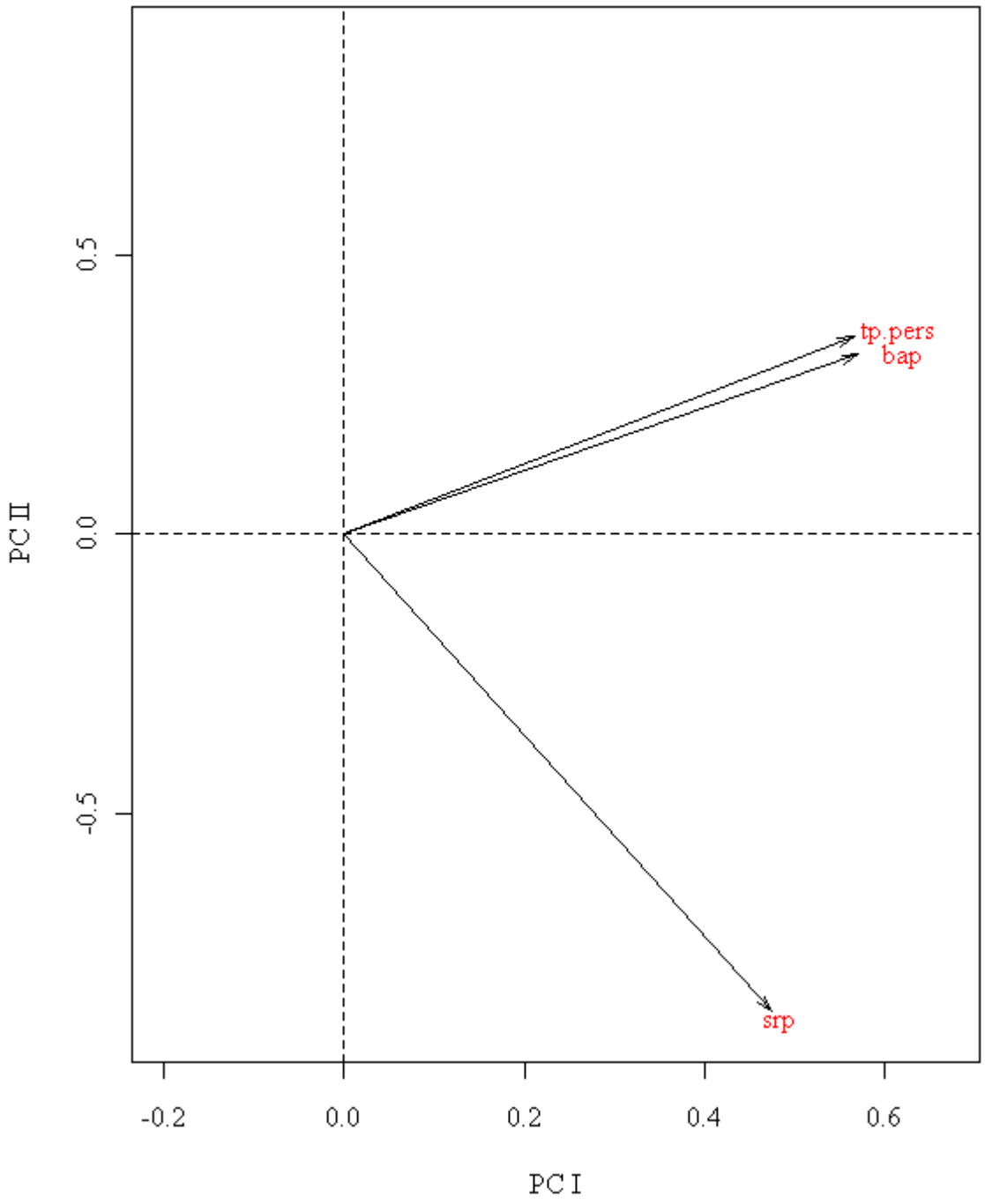

Figure A10. Variable loadings for srp, bap, and tp_{pers} variables. The first component was composed of bap and tp_{pers}, while the second component was solely composed of srp.

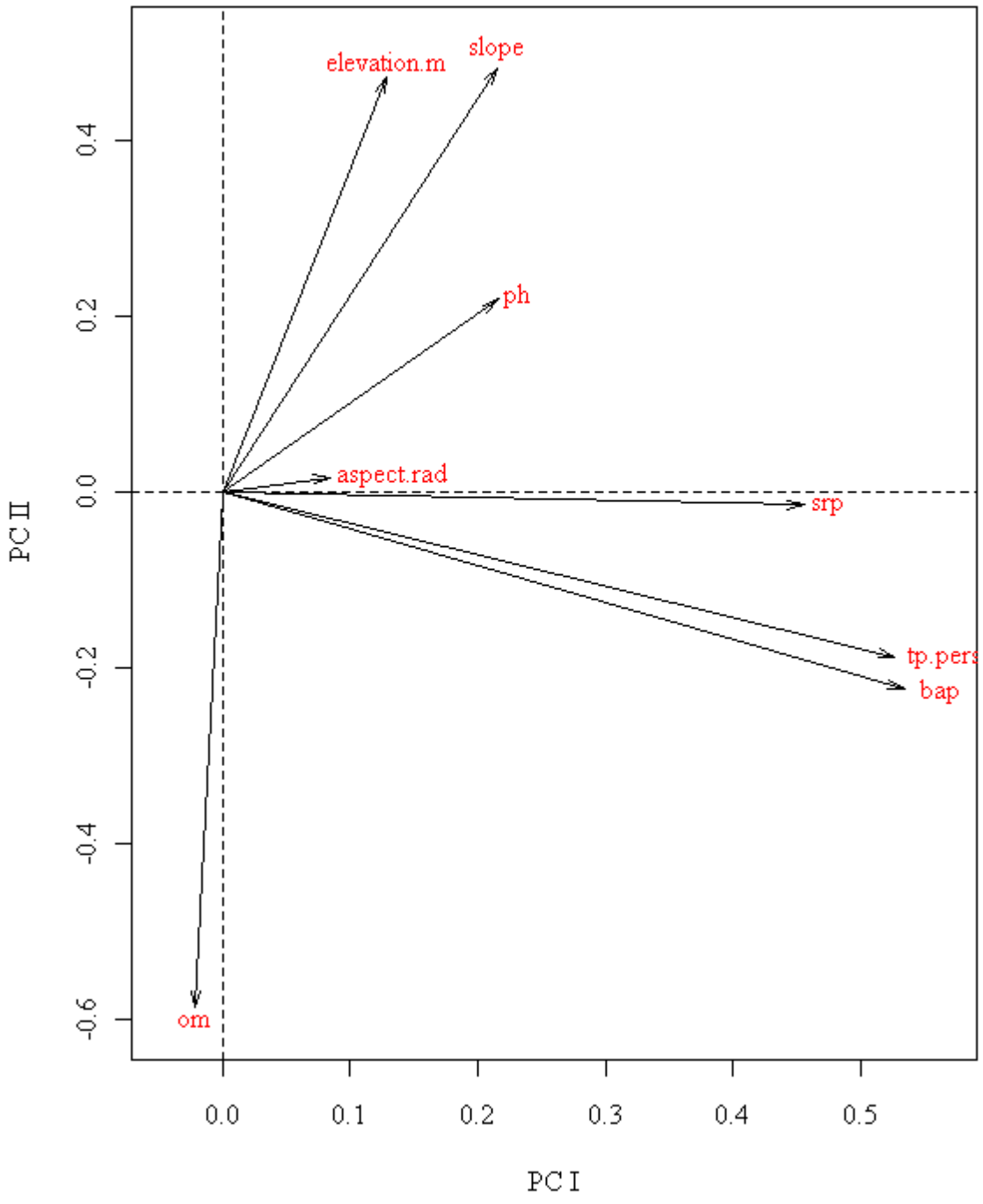

Figure A11. Variable loadings for aspect, elevation, om, slope, srp, bap, and tp_{pers}. The first component was largely influenced by phosphorus while the second component was influenced by the combination of slope and elevation contrasted against om.

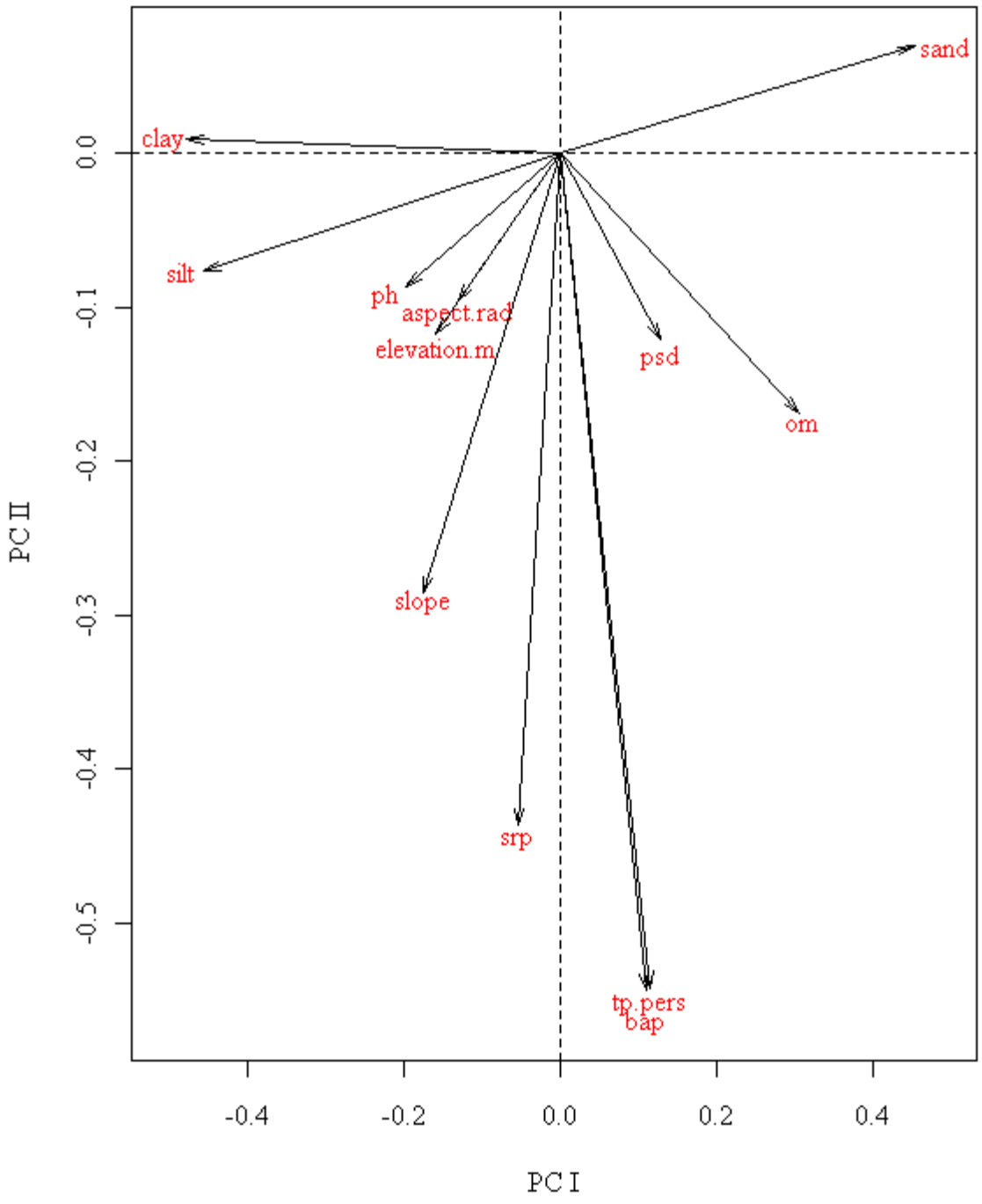

Figure A12. Variable loadings for aspect, elevation, om, slope, srp, bap, tp_{pers}, particle size, sand, silt and clay. The first component was composed of fine particulates (clay and silt), while the second component was mostly influenced by phosphorus.

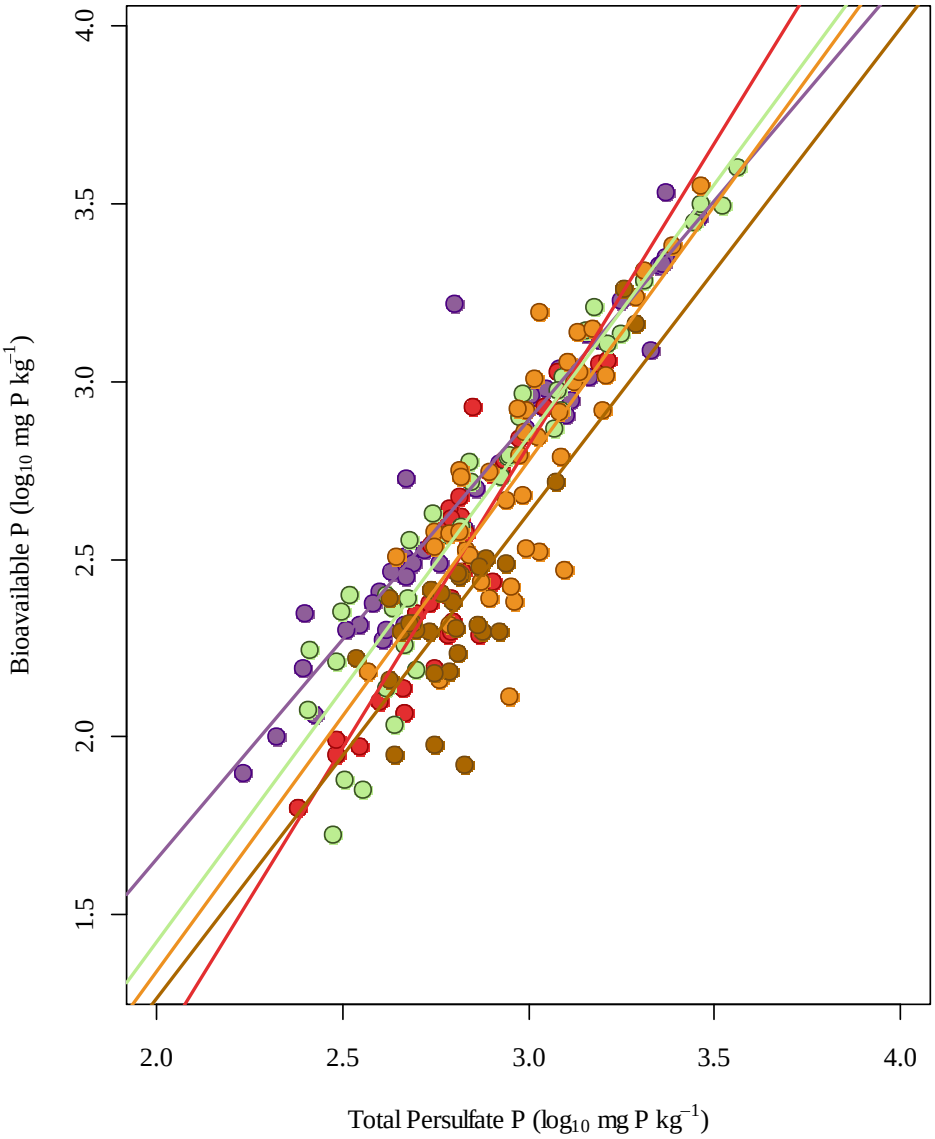

Figure A13. Linear regression models of bap as a function of tp_{pers} for individual soil series. Some models are highly predictive of bap while others are less powerful, although all are statistically significant.

Soil Type	Slope	Intercept	Adj. R^2
Chuckanut	1.233	−0.807	0.909***
Sehome	1.704	−2.290	0.809***
Squalicum	1.422	−1.422	0.902***
Squires	1.437	−1.535	0.644***
Wickersham	1.364	−1.462	0.630***

*** P-value < 0.001

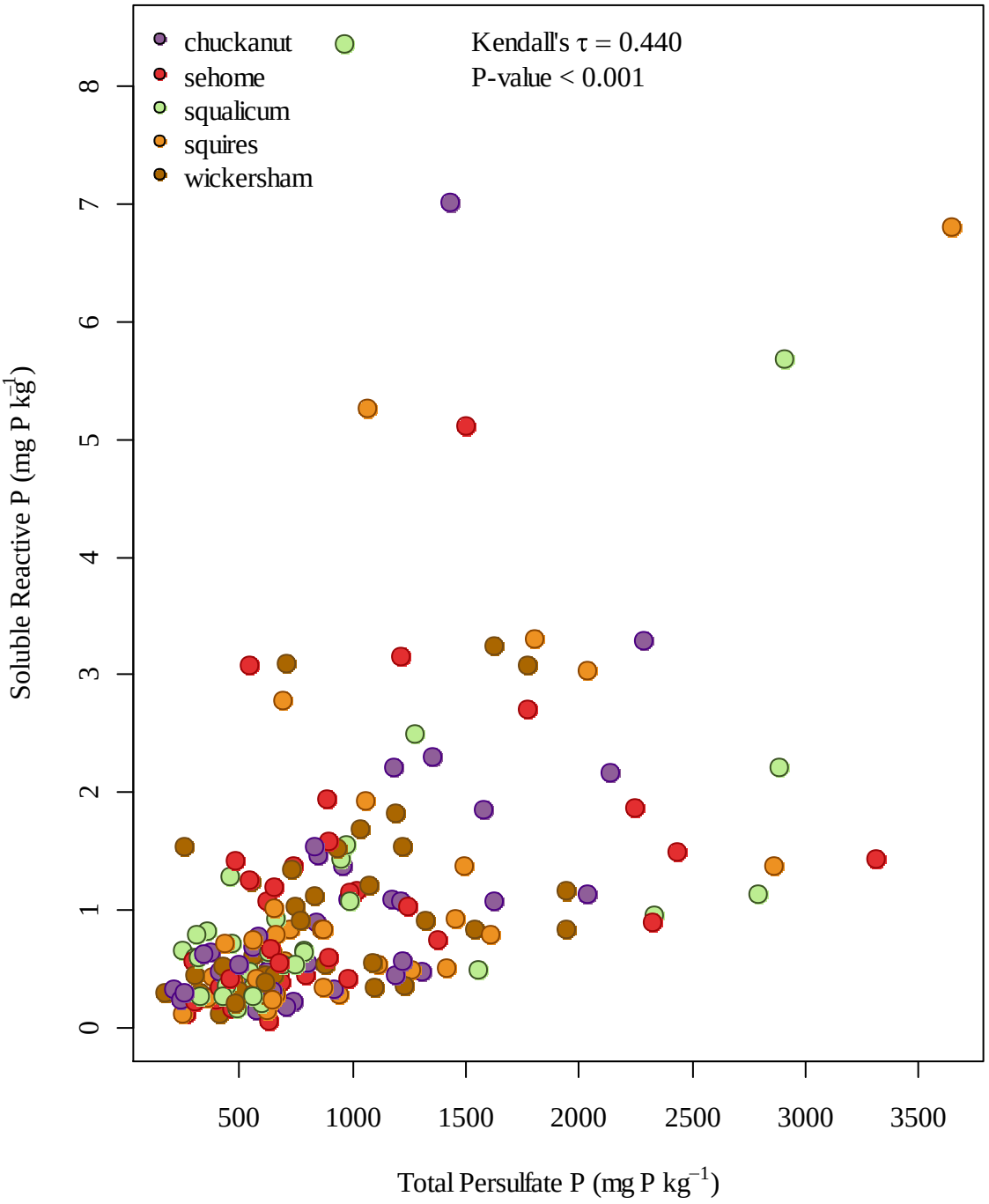

Figure A14. Association between SRP and TP_{pers} in soil samples from the Lake Whatcom watershed.

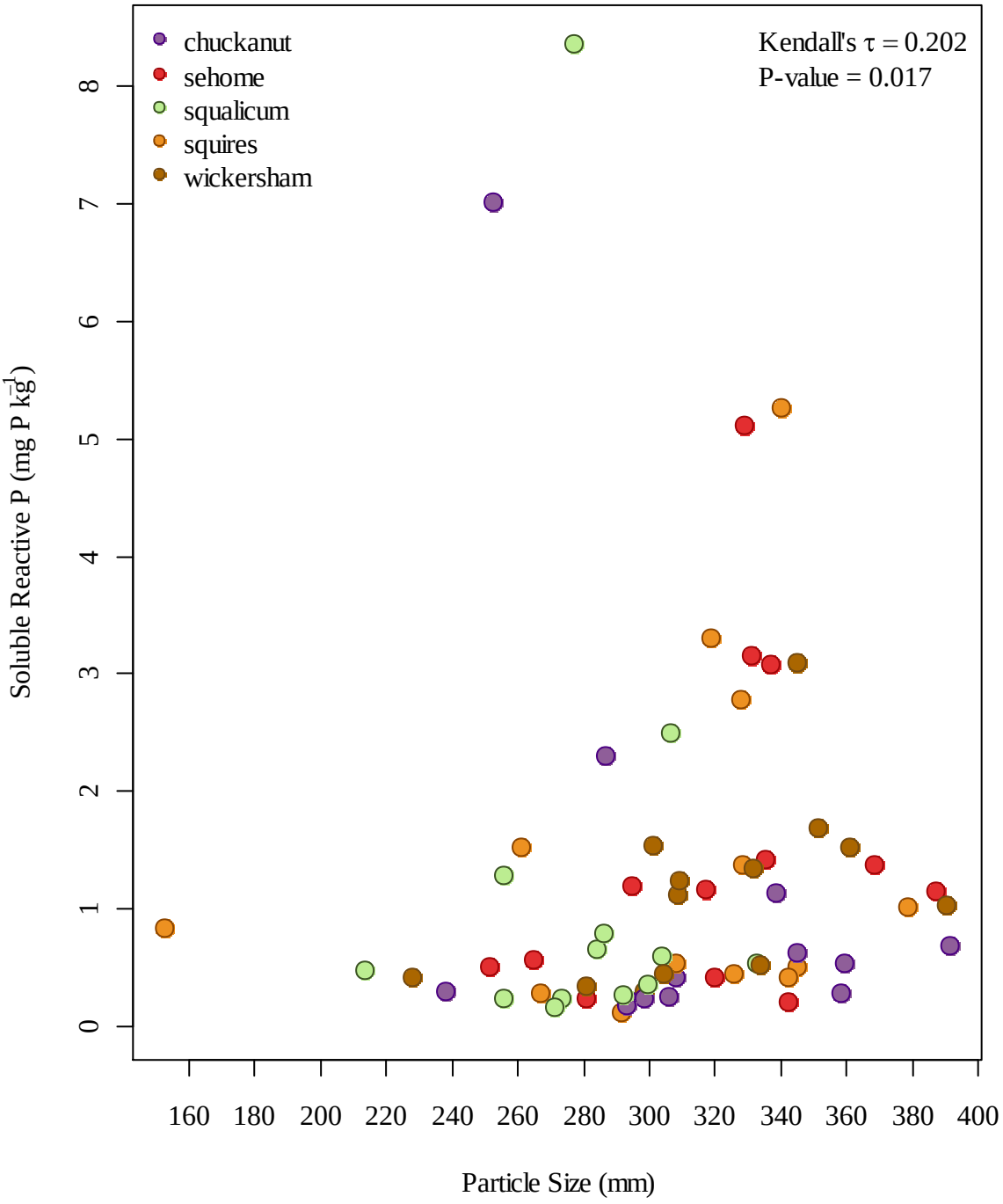

Figure A15. Association between SRP and median particle size in soil samples from the Lake Whatcom watershed.

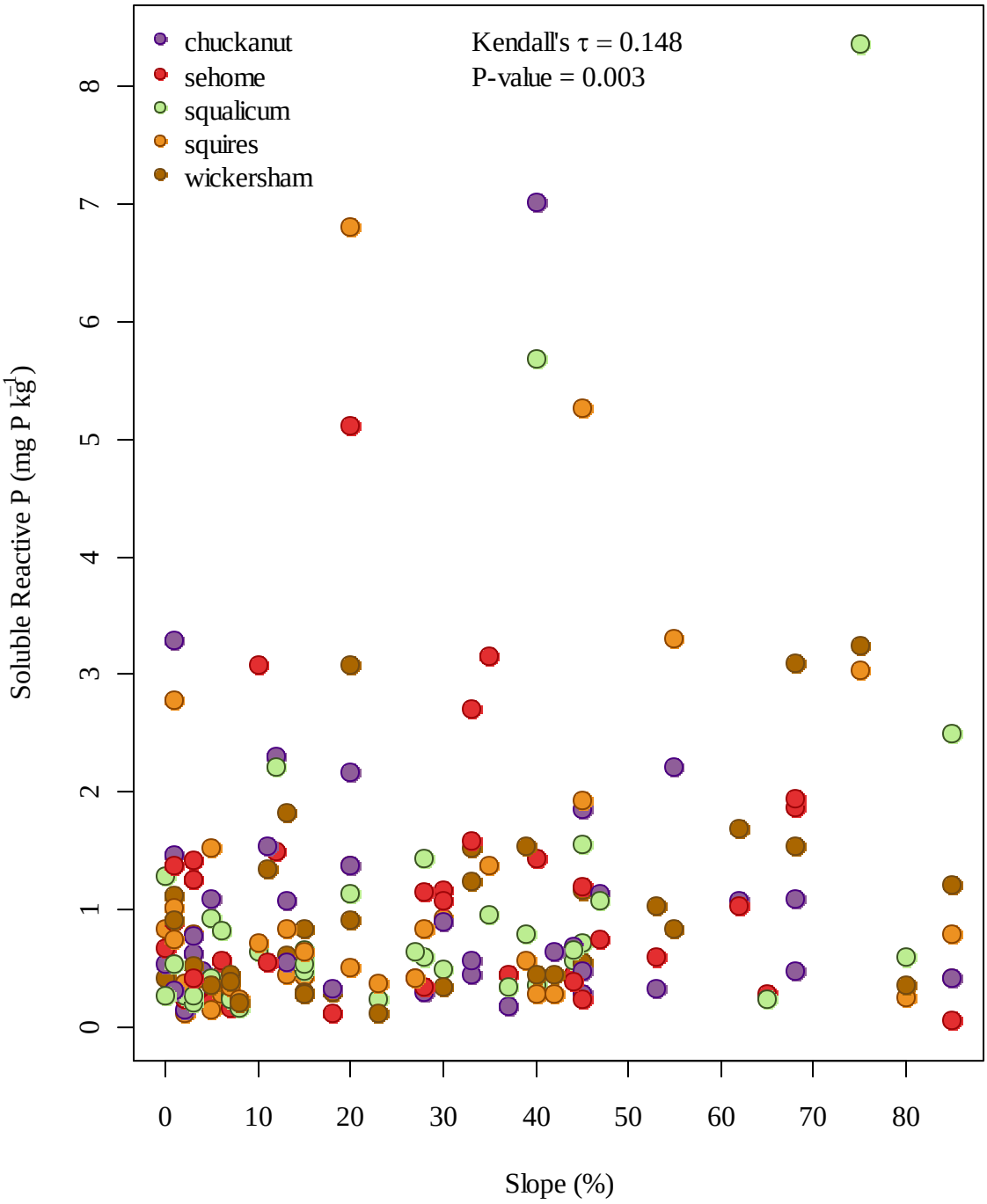

Figure A16. Association between SRP and slope in soil samples from the Lake Whatcom watershed.

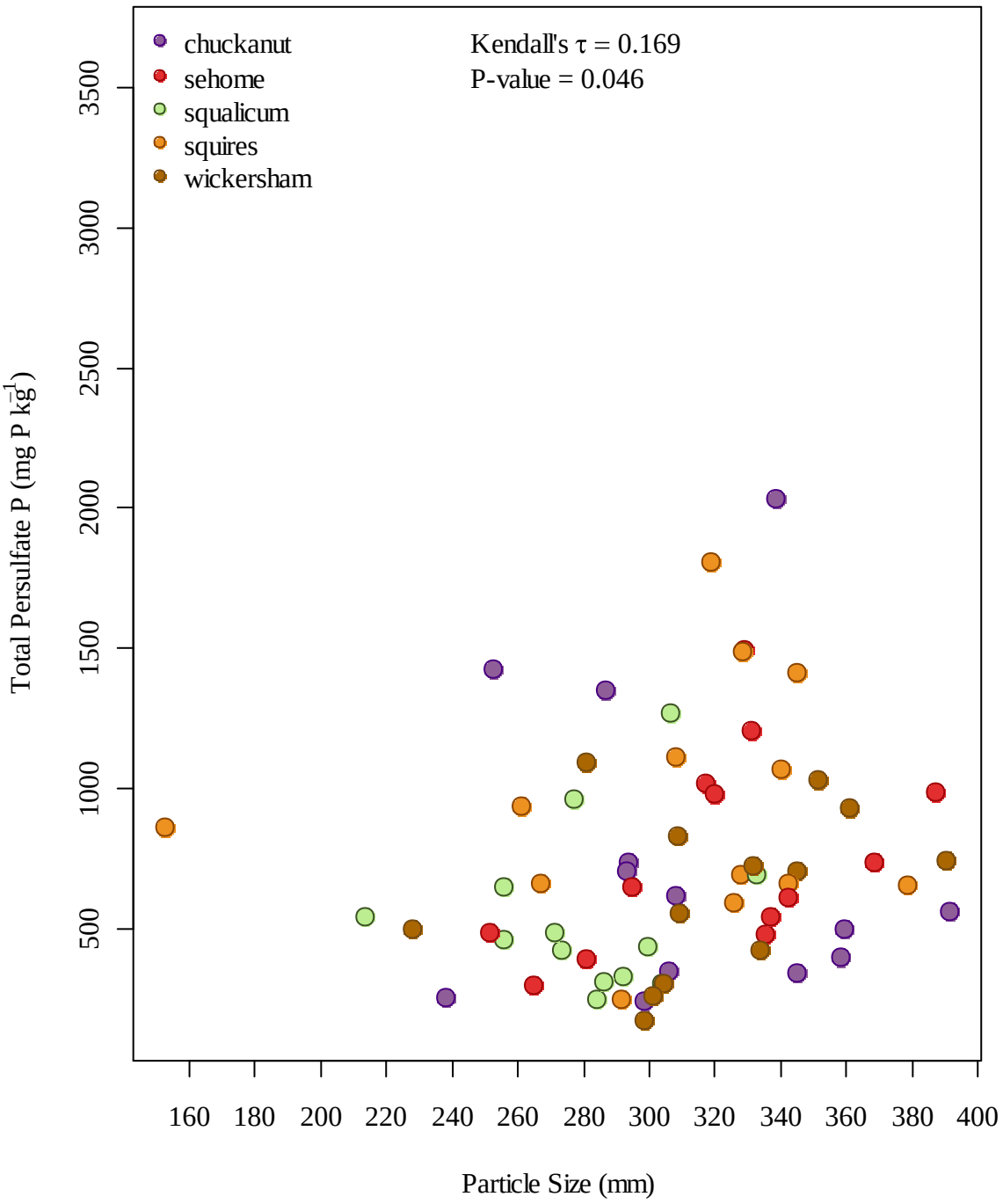

Figure A17. Association between TP_{pers} and median particle size in soil samples from the Lake Whatcom watershed.

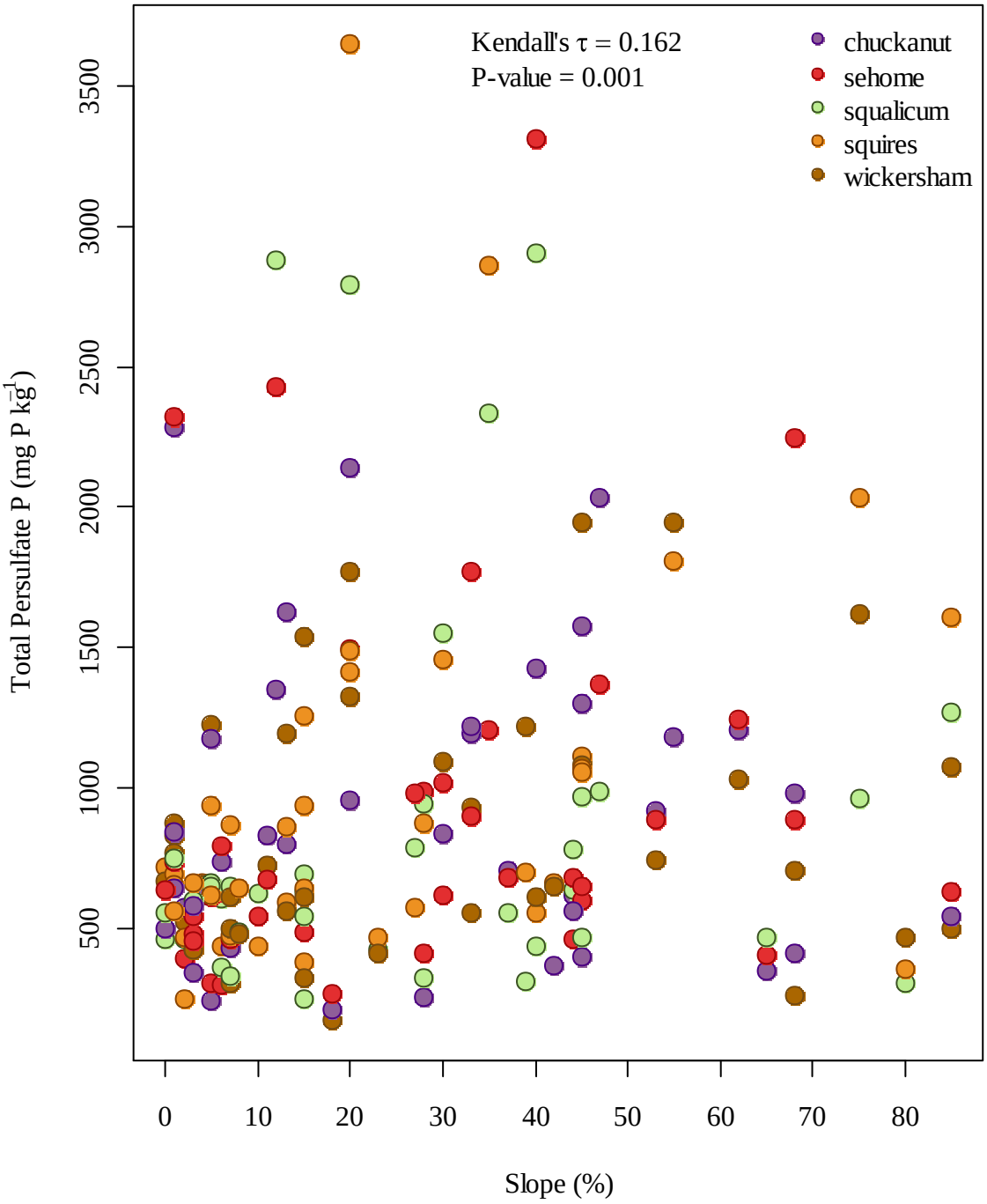

Figure A18. Association between TP_{pers} and slope in soil samples from the Lake Whatcom watershed.

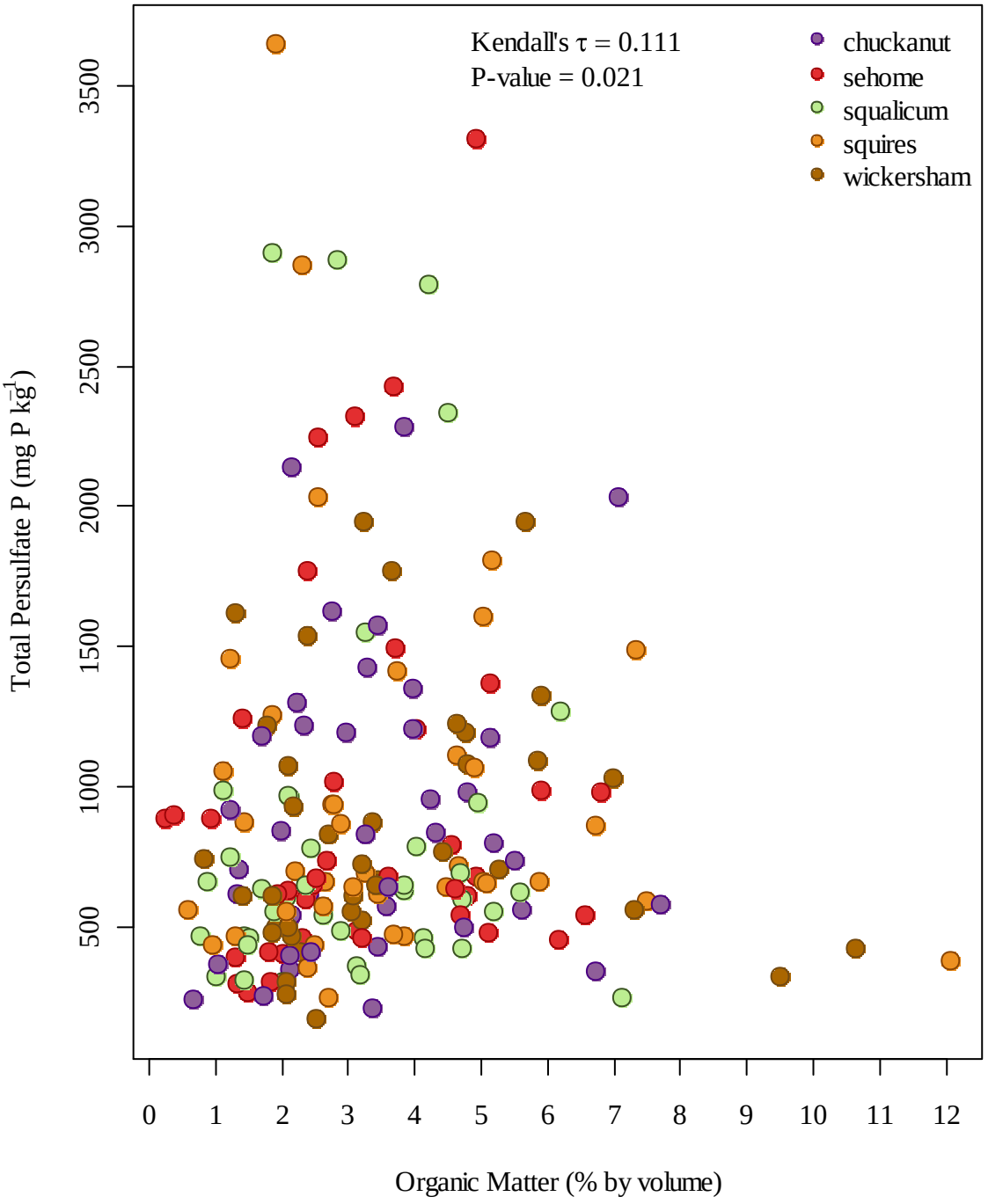

Figure A19. Association between TP_{pers} and organic matter in soil samples from the Lake Whatcom watershed.

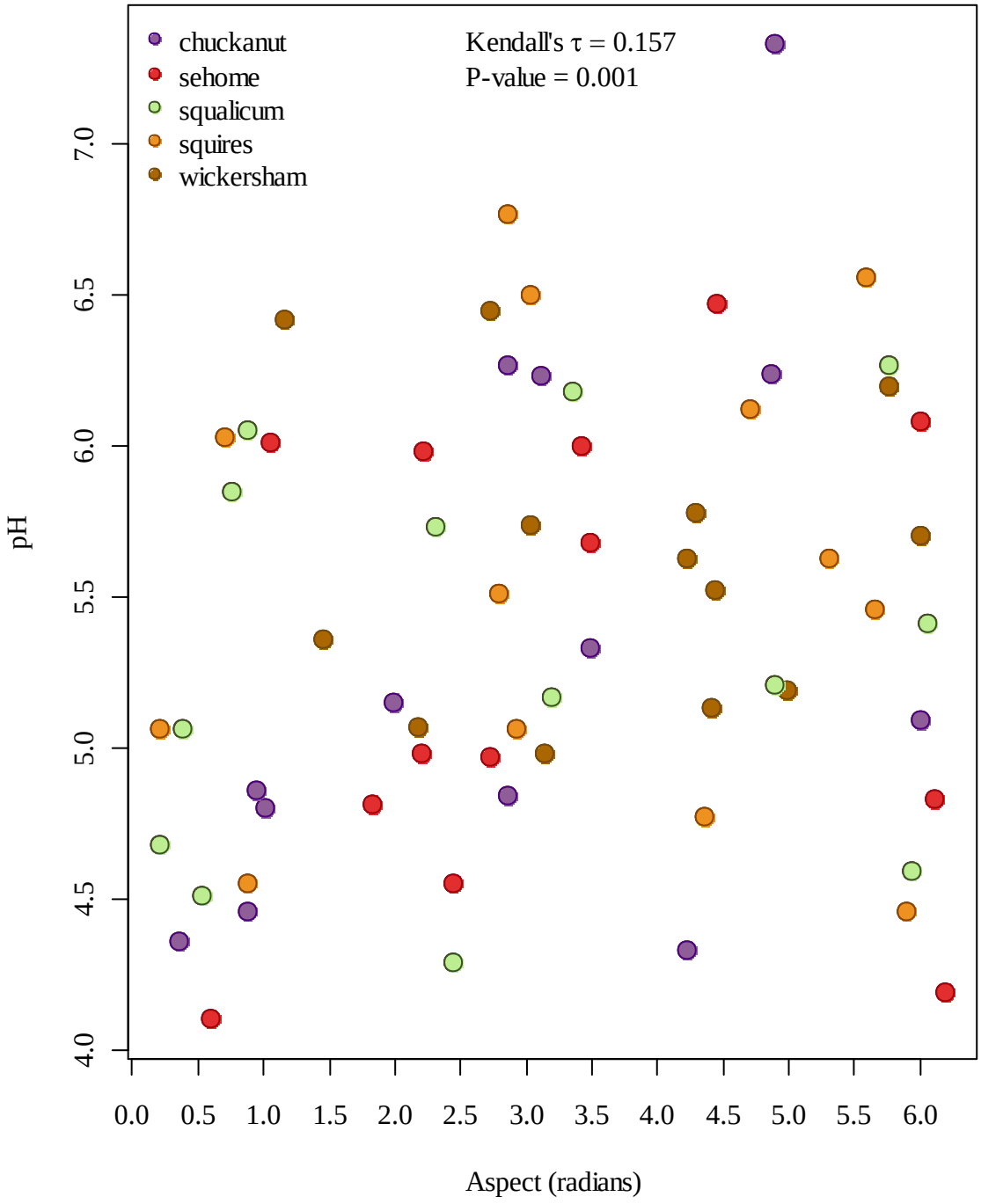

Figure A20. Association between pH and aspect in soil samples from the Lake Whatcom watershed.

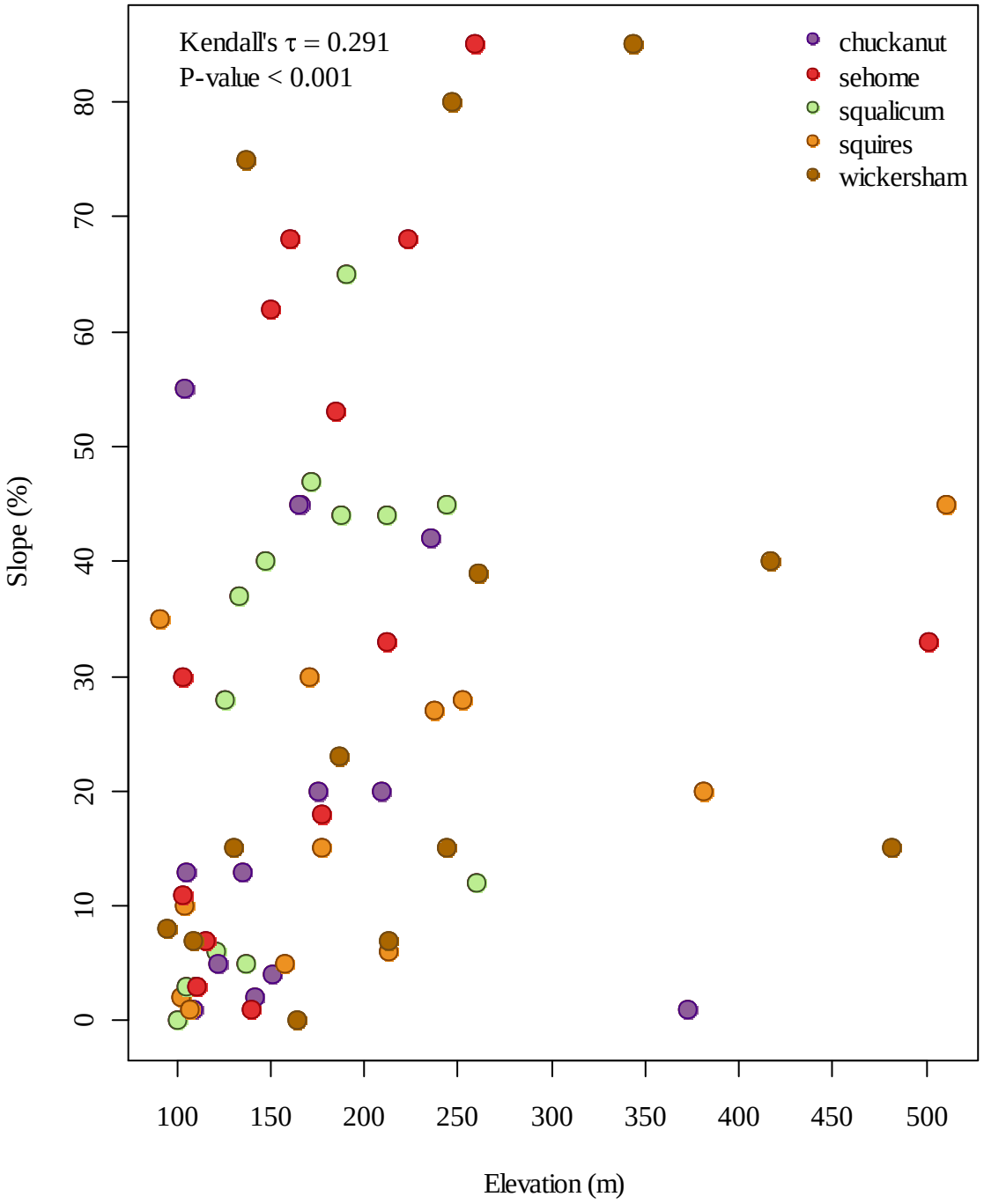

Figure A21. Association between slope and elevation in soil samples from the Lake Whatcom watershed.

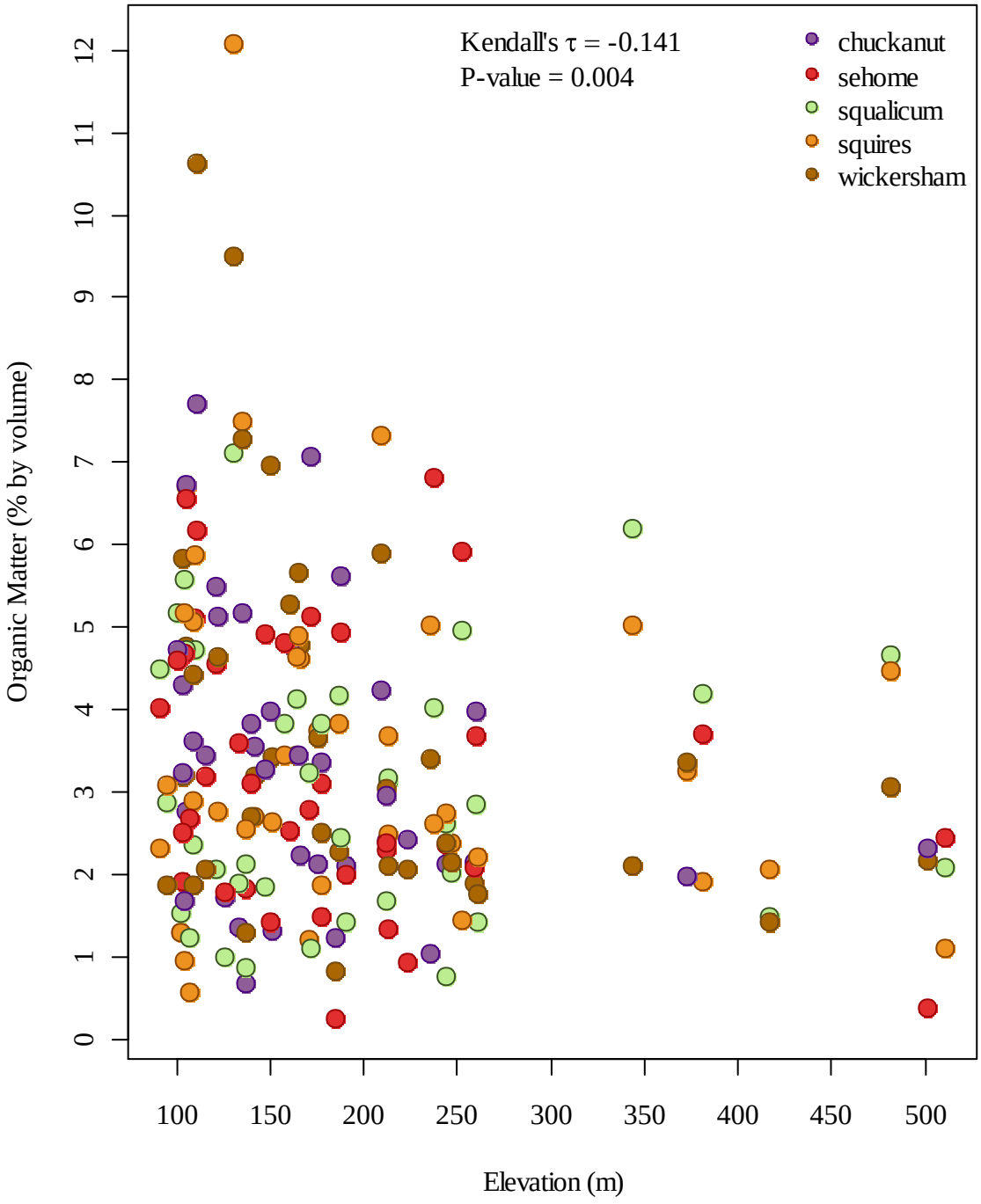

Figure A22. Association between organic matter and elevation in soil samples from the Lake Whatcom watershed.

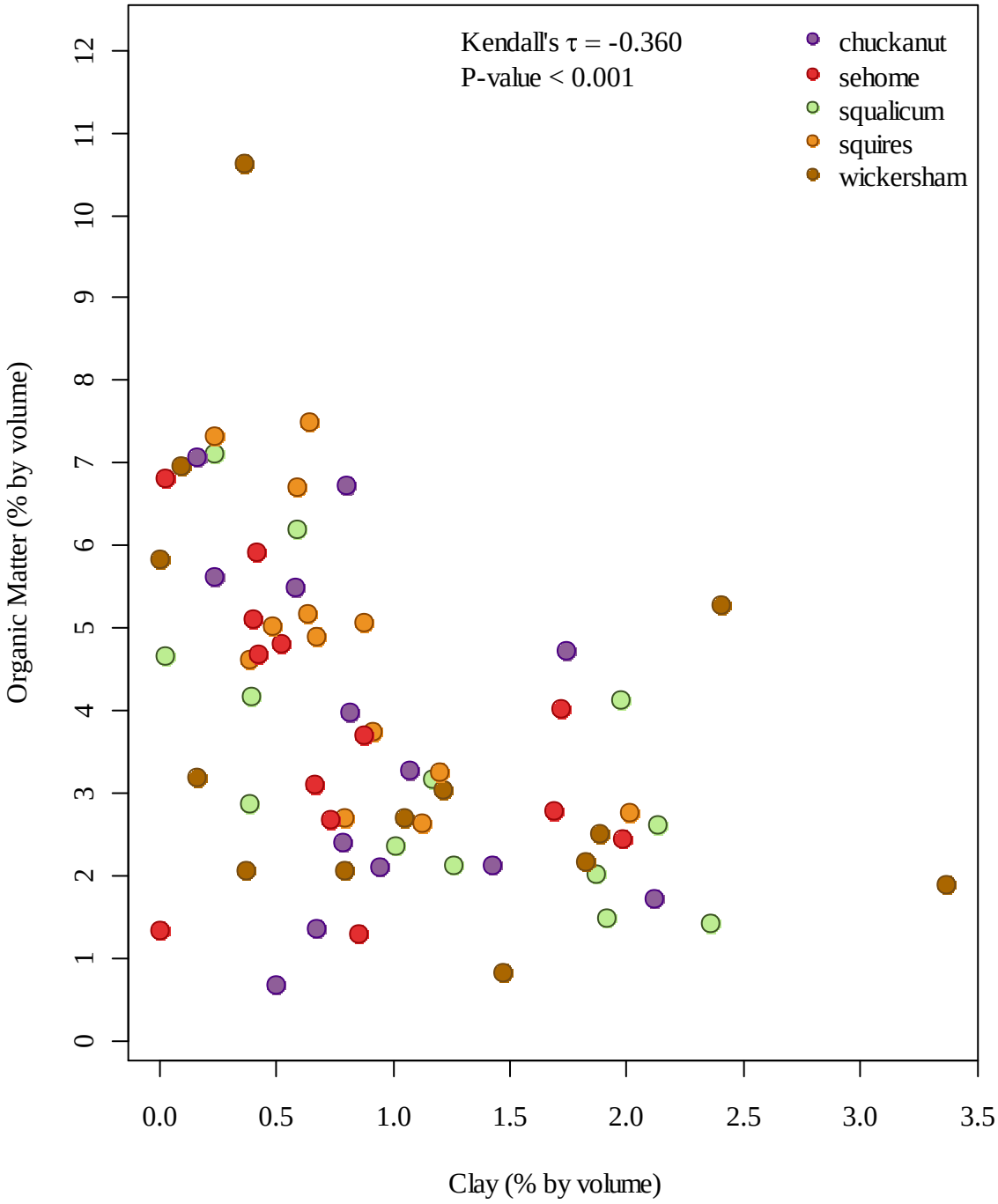

Figure A23. Association between organic matter and clay in soil samples from the Lake Whatcom watershed.

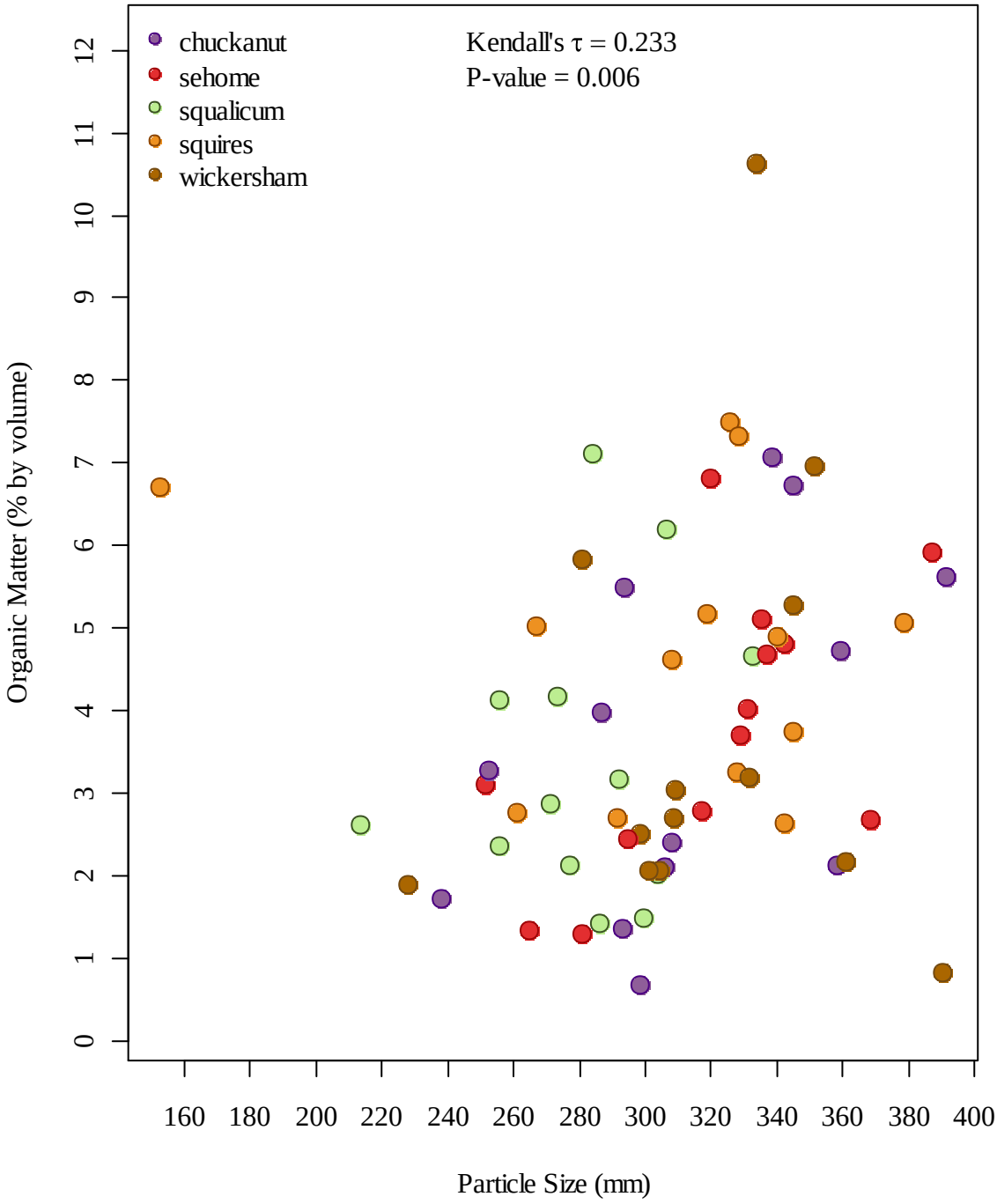

Figure A24. Association between organic matter and median particle size in soil samples from the Lake Whatcom watershed.

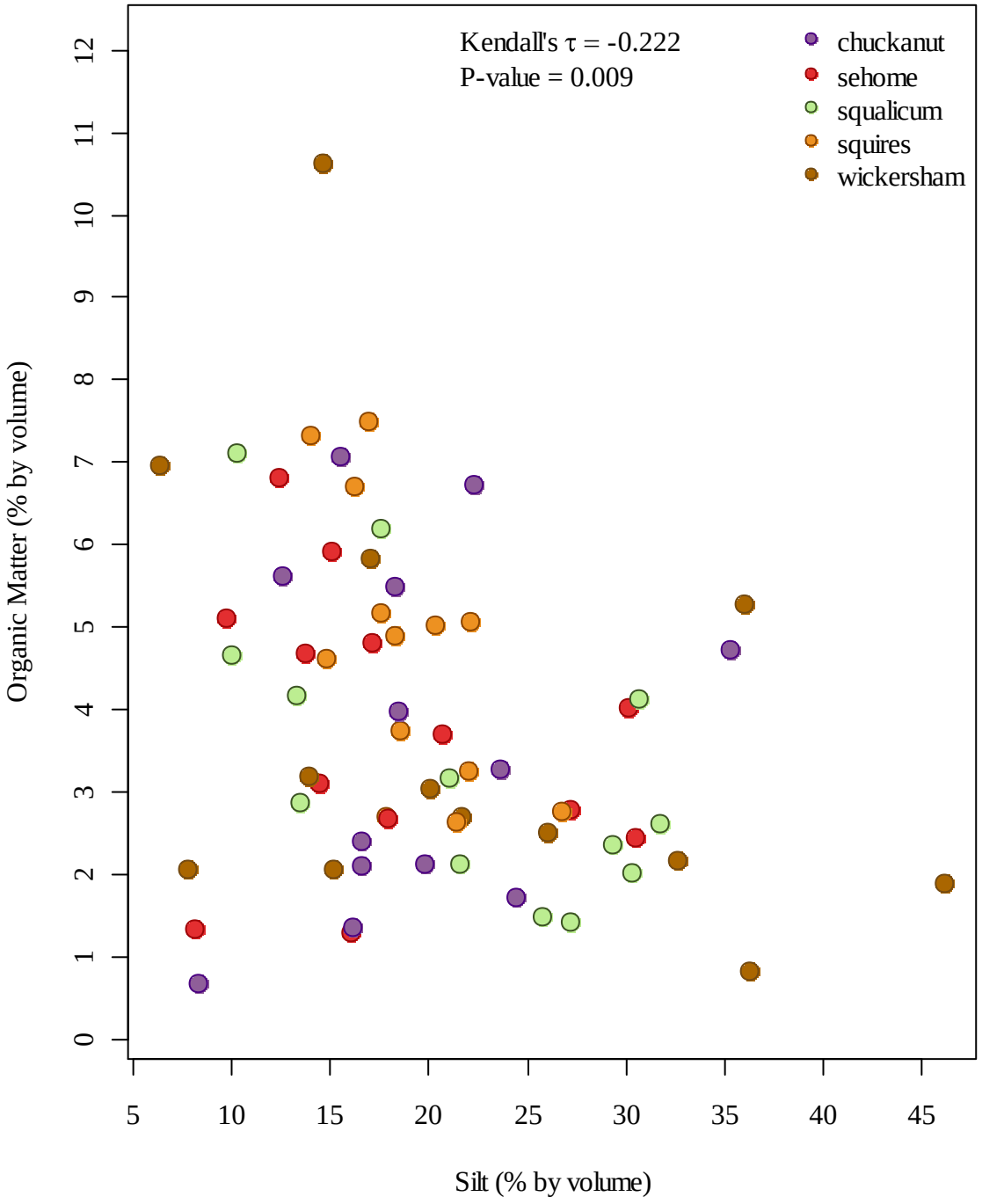

Figure A25. Association between organic matter and silt in soil samples from the Lake Whatcom watershed.

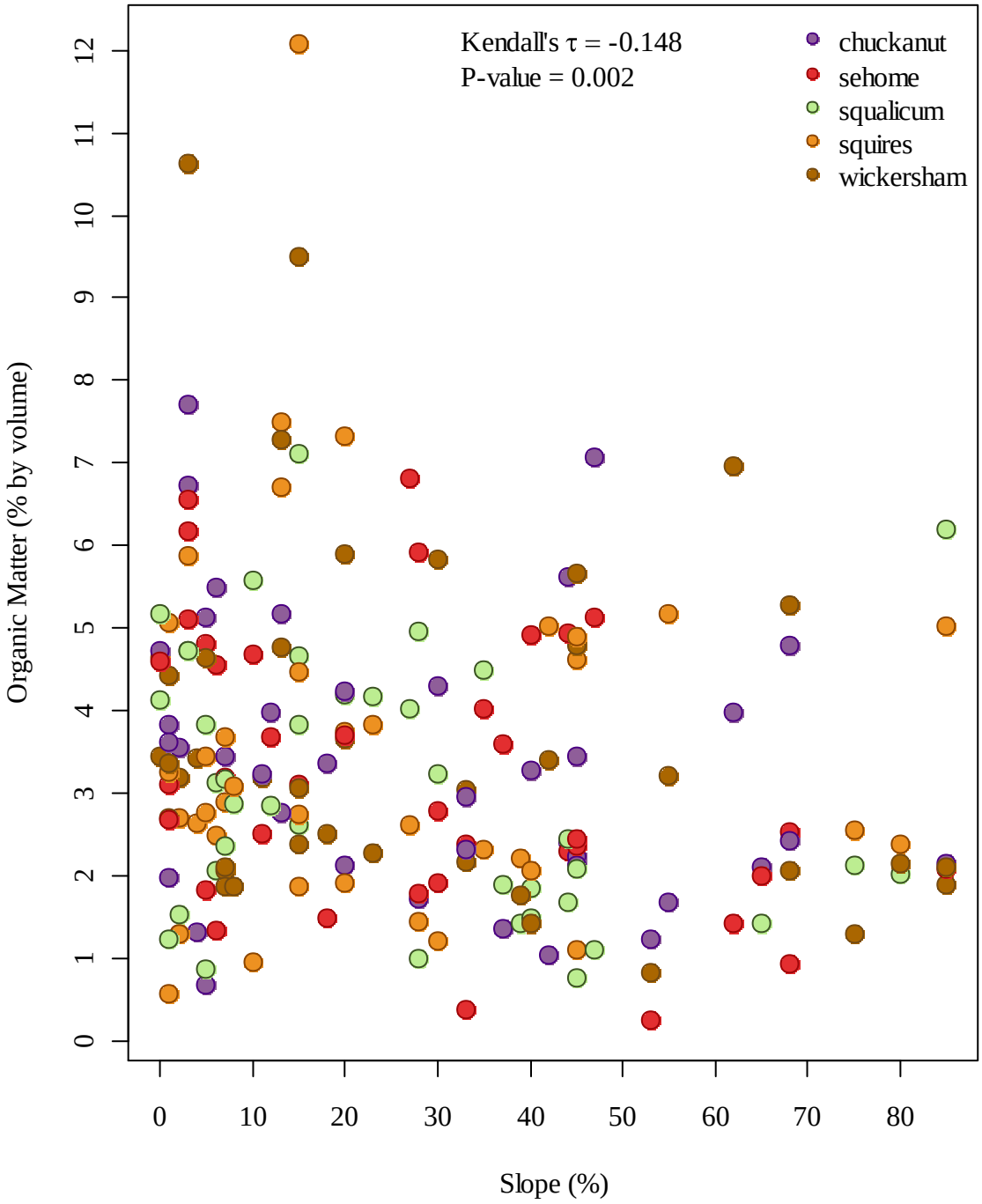

Figure A26. Association between organic matter and slope in soil samples from the Lake Whatcom watershed.

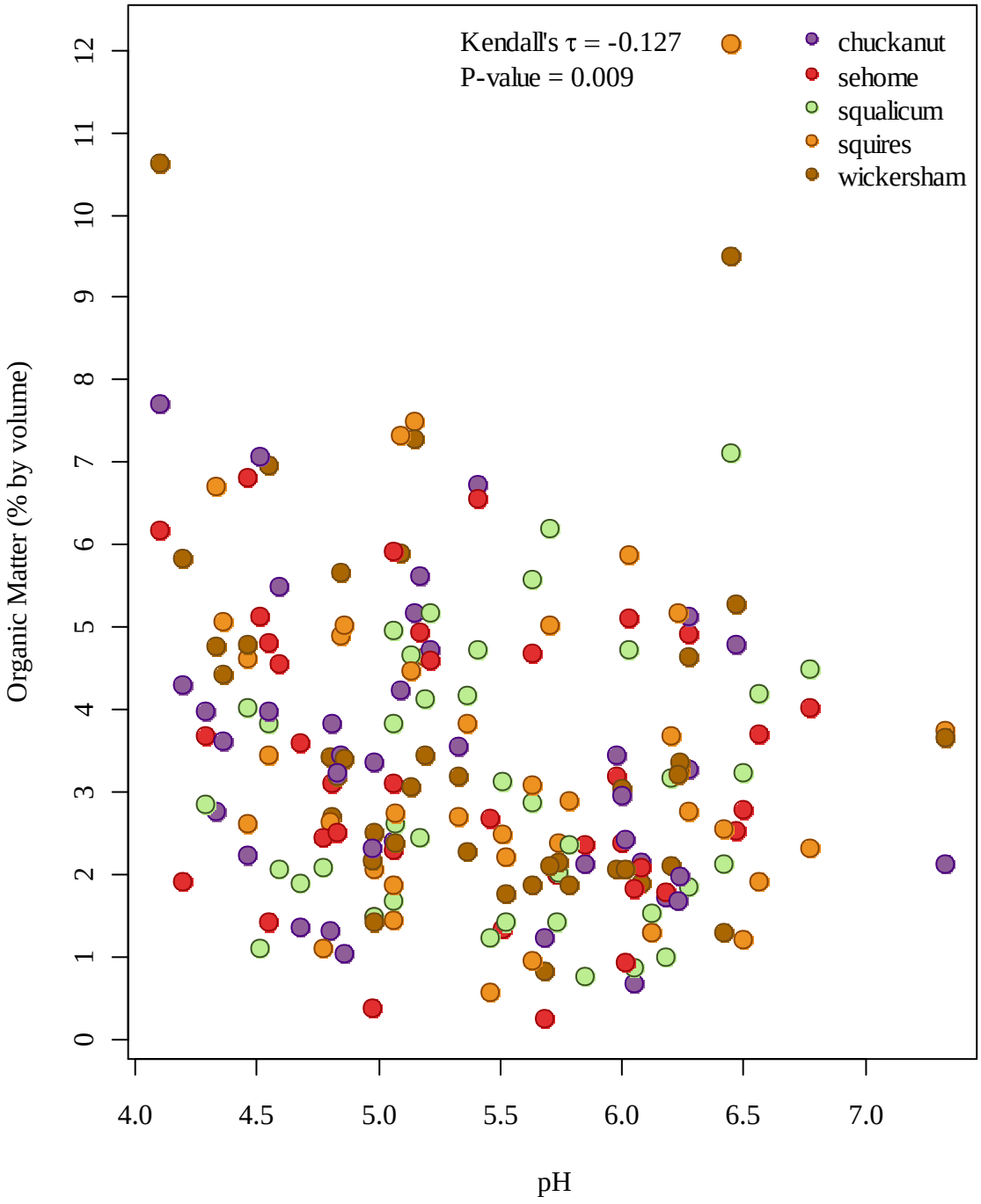

Figure A27. Association between organic matter and pH in soil samples from the Lake Whatcom watershed.

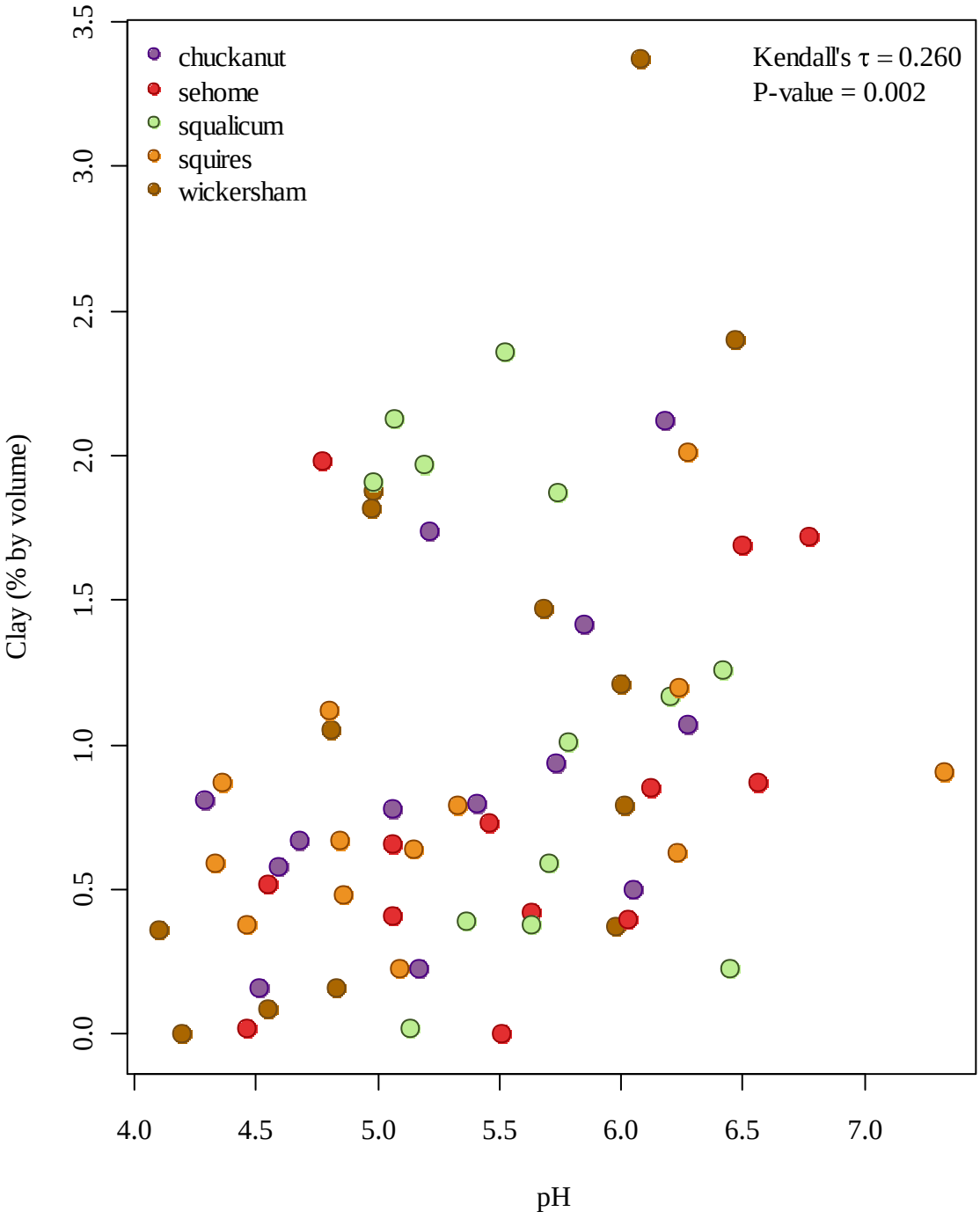

Figure A28. Association between clay and pH in soil samples from the Lake Whatcom watershed.

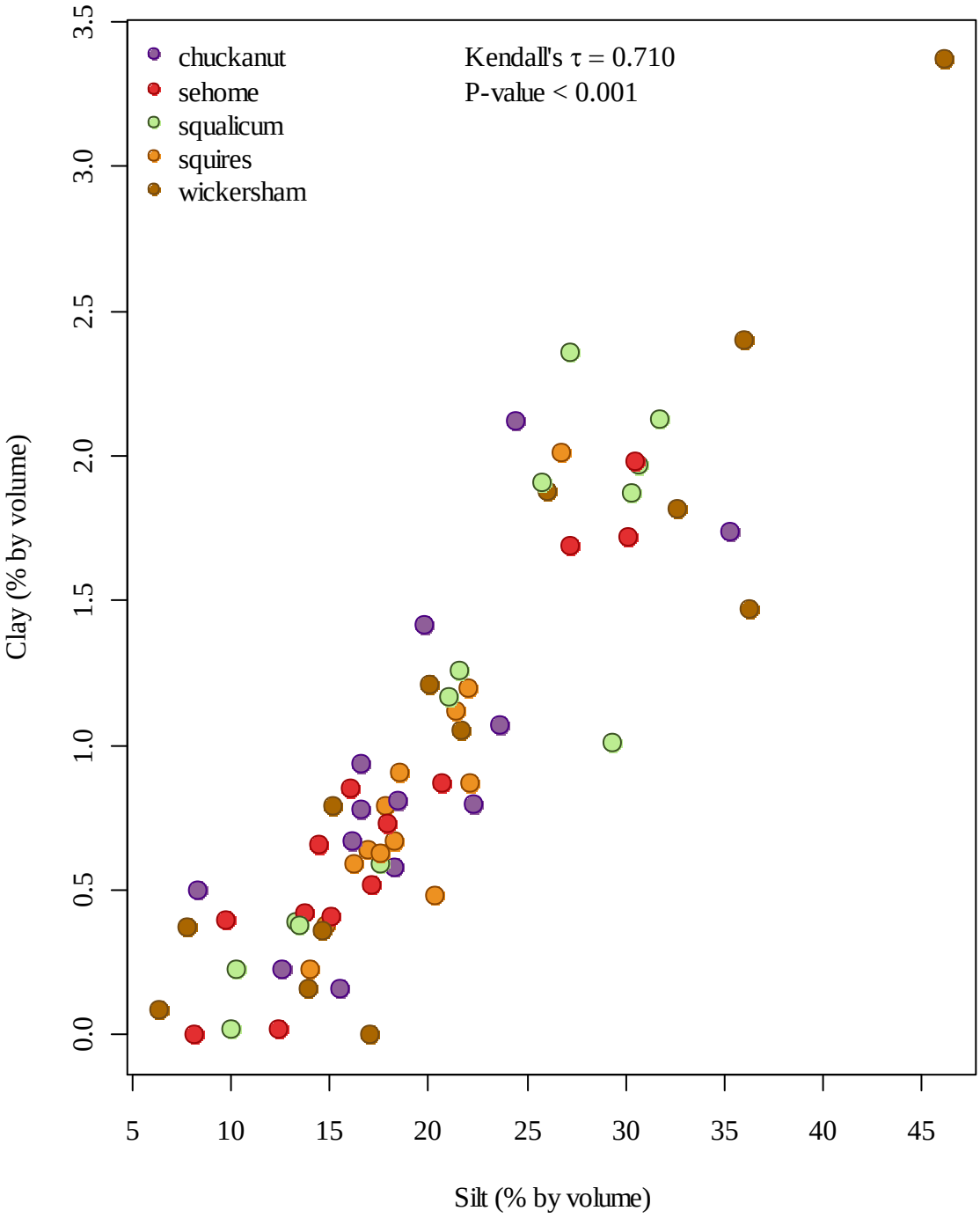

Figure A29. Association between clay and silt in soil samples from the Lake Whatcom watershed.